I. THE MAGNETIC SUSCEPTIBILITY OF EUROPIUM(III) AND EUROPIUM(II) IONS AND THE PHOTOCHEMICAL REDUCTION OF WATER BY EUROPIUM(II) ION

II. THE MAGNETIC SUSCEPTIBILITY OF EUROPIUM AND SAMARIUM AMALGAMS

III. OBSERVATIONS ON THE CHEMISTRY OF EUROPIUM

IV. AGE DETERMINATION FROM CARBON-14 CONTENT: IONIZATION CHAMBER TECHNIQUES

V. THE VOLUME CHANGE DUE TO HYDROGEN BONDING OF METHANOL IN CARBONTETRACHLORIDE SOLUTION

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ABSTRACT

The discovery of the photochemical reduction of water by europium(II) ion is reported. By use of a chemical actinometer for determining light intensities and a Gouy balance for following the change in magnetic susceptibility overall quantum yields were determined to be about 0.2 for solutions 0.5 m. in HCl and 0.15 m. in $EuCl_2$. A mechanism consistent with the experimental data is

$$Eu(II)\cdot H_2O + h\nu = Eu(II)^*\cdot H_2O$$

$$Eu(II)^*\cdot H_2O = Eu(III)_{aq} + H + OH^-_{aq}$$

$$H + H^+_{aq} + Eu(II)_{aq} = Eu(III)_{aq} + H_2$$

The thermal reaction under these conditions was found to be relatively unimportant.

The magnetic susceptibility of europium in its liquid amalgam was observed to be 8.09 ± 0.03 Bohr magnetons and that of samarium in its liquid amalgam to be 2.31 ± 0.05 Bohr magnetons.

In a brief investigation europium(II) perchlorate was observed to be quite soluble in water and the solution stable as regards oxidation of the europium. The preparation of europium(II) carbonate is discussed. The possible reduction of CO_2 by the hydrogen atoms produced in the irradiation of Eu(II) solutions was investigated, negative results being obtained.

Using an ionization chamber in conjunction with a very sensitive quartz fiber electroscope, the small amount of C^{14} present in "living" carbon was detected. The problem of background ionization observed in the chambers was investigated in detail. Preliminary experiments to determine the suitability of the instruments for the measurement of the age of archeological specimens were carried out. The age of one specimen was

observed to be about 3,500 years.

The densities of dilute solutions of CH_3OH in CCl_4 are reported. A comparison of the partial molar volumes obtained therefrom with the monomer fraction of CH_3OH determined by spectroscopic means leads to the conclusion that the average volume of the monomer is only 2% greater than that of the CH_3OH in the polymers.

TABLE OF CONTENTS

PART I

THE MAGNETIC SUSCEPTIBILITY OF EUROPIUM(III) AND EUROPIUM(II) IONS AND THE PHOTOCHEMICAL REDUCTION OF WATER BY EUROPIUM(II) ION*

Introduction

As with scientific activity in general, the study of the physical and chemical properties of the rare-earth elements and their compounds has shown a marked increase in the last few years. From a chemical point of view the most interesting of these elements are those which display "anomalous" oxidation states, i.e., oxidation states other than three (2). Europium is one of these, compounds of both plus three and plus two europium having been prepared.

Urbain and Bourion were the first to prepare a compound of europium (II) (3). By passing a mixture of S_2Cl_2 and Cl_2 over $EuCl_3$, kept just below its melting point, they obtained a mixture of $EuCl_3$ and $EuCl_2$. A fairly pure $EuCl_2$ was obtained by passing a slow stream of H_2 over $EuCl_3$ heated to 400-500° C. For nearly two decades after that the study of europium(II) compounds was neglected; the next work reported is that of Jantsch, Alber and Grubitsch in 1929 (4). These investigators repeated the work of Urbain and Bourion and also prepared EuI_2 by passing a mixture of HI and H_2 over $EuCl_3$ at high temperature. They also prepared europium(II) sulfate by adding Na_2SO_4 to a solution of $EuCl_2$. In 1930 Yntema obtained pure $EuSO_4$ by electrolytically reducing europic chloride

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* Some of the results reported in this section have been published as a Letter to the Editor in the J. Chem. Phys. (1).

solutions containing sulfate ion (5). McCoy discovered that europium can be conveniently reduced to the bivalent state by passing solutions through a Jones reductor containing amalgamated zinc (6). Using this method as the basis of a separation from the rest of the rare-earths, McCoy isolated about two kilograms of exceedingly pure Eu_2O_3 - by no means the least of his contributions to the chemistry of europium. Other compounds of bivalent europium which have been prepared and studied are: EuF_2 and $EuBr_2$ (7), $EuCO_3$ (8), EuS (9), EuSe and EuTe (10). All of the compounds mentioned are stable in contact with dry air. However, most, if not all, when wet are readily oxidized by oxygen.

It is clear from the above that the "dry" chemistry of europium(II) compounds is fairly well known. The solution chemistry is much less well understood. Thus the object of this research is the investigation of the properties of europium(II) compounds in aqueous solution. Early investigators noted the marked reducing power of such solutions. In this connection McCoy has determined the europium(II)-europium(III) potential to be +0.43 volts (6). Noddack and Brukl (11) and also Laitenen and Taebel (12) have measured this potential by polarographic means, the former reporting + 0.46 volts and the latter + 0.425 ± 0.002 volts. It is not surprising that these solutions are rapidly oxidized when exposed to air. McCoy found that a 0.05 f. solution of $EuCl_2$ is half oxidized by a rapid stream of air in about five minutes (6). Since the literature contains several reports to the effect that europium(II) ion is slowly oxidized by water with the evolution of hydrogen (13, 14, 15), it was decided to make a careful study of this reaction. The work of R. A. Cooley (15) suggested following the course of the reaction by observing the attending

change in magnetic susceptibility with a Gouy balance (16, 17). This method has the distinct advantage of obviating the necessity of removing samples of the solutions for analysis. Thus, if the total europium concentration is known, the concentrations of the two species can be readily determined by measuring the magnetic susceptibility of the solution.

Preliminary experiments soon led to the discovery of a photochemical reduction of water by europium(II) ion. It was found that solutions 0.25 m. in europium(II) chloride and 0.3 m. in hydrochloric acid were stable over periods of weeks when kept in the dark, but evolved hydrogen* rapidly when exposed to bright light (either sunlight or a tungsten projection lamp). Experiments were then directed toward a determination of the quantum yield of the photochemical reaction. Concurrently careful measurements of the susceptibilities of europium(III) and europium(II) ions were carried out. Solutions of $EuCl_2$ in hydrochloric acid were used exclusively in the photochemical experiments. Undesirable solubility relationships or the possibility of other reactions prohibited the use of other common acids.

Experimental

The europium used came originally from the stock of the late Dr. H. N. McCoy. Mrs. Ethel T. McCoy was kind enough to augment the supply with a loan of more of the same material. A spectrographic check of its purity was made with the Applied Research Laboratories Grating Spectrograph (dispersion of 7 Å per mm.). None of the lines of the neighboring

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* Colorless, odorless combustible gas.

rare-earths were found. However, traces of calcium and magnesium were revealed to be present. This result is in agreement with that reported by McCoy (18).

For the magnetic measurements essentially the same Gouy balance as is described by Whittaker was employed (19). Currents of 11 and 13 amps. were used, giving fields of about 8600 and 9100 oersteds, respectively. One noteworthy improvement was the provision of a selenium rectifier to dissipate safely, on opening the switch, the energy stored in the magnetic field. This rectifier served to give maximum protection to the insulation of the magnet coils during normal operation and in case of accidental opening of the circuit. The sample tubes were of the usual partition type - provided at the top with a cap fitted with a micro-stopcock (H, Figure 3). Both the bottom of the cap and the top of the tube were ground flat and a seal was effected with Apiezon "W" wax. With regard to the calibration of the equipment the same procedure was followed as is described by Whittaker. Six sample tubes were constructed and an "apparatus constant" obtained for each one. All experiments were carried out with 12.0 ± 0.2 ml. of solution; and this volume of nickel chloride solution was used in the calibration. The dimensions of the tubes were such that the meniscus was well out of the strong field; and the small changes in its position, caused by the slight variations in volume of solution, did not affect the results. The tube partition was centered between the pole pieces with the aid of a cathetometer.

As mentioned above a number of preliminary experiments were carried out to determine under what conditions, if any, solutions of europium(II) chloride are stable. In most of these the solutions were made up by adding

hydrochloric acid to europium(II) carbonate. The $EuCO_3$ was prepared by the method described in Part III of this thesis and also by the method of Cooley and Yost (8). At this time a "dry box" was not available for carrying out the filtering and washing operation in a CO_2 atmosphere, and the products varied from 80-90% $EuCO_3$. Analyses were made by the method of McCoy in which the europium(II) compound is added to a solution containing an excess of $Fe_2(SO_4)_3$ in 1.8 n. H_2SO_4 and the resulting iron(II) ion is titrated with permanganate (20). In the later experiments the solutions were prepared using $EuCl_2$. This was made in the usual manner by passing a mixture of H_2 and HCl over $EuCl_3$ in a quartz tube maintained at about 700° C. The apparatus was quite similar to that described by Cooley and Yost (8), except that tank HCl was employed. The anhydrous $EuCl_3$ was prepared by carefully dehydrating the hexahydrate in an atmosphere of HCl and N_2 (21). The first few preparations were analyzed by determining the chloride as AgCl. It was found that complete reduction could be achieved at 700° C. in four hours.

In a typical experiment the filling of the Gouy tube was achieved as follows: The rim of the clean, dry tube was coated with Apiezon "W" wax and the tube and cap weighed. The tube was then placed in position as shown in Figure 1. The solution to be used was prepared in a 100 ml. volumetric flask by weighing in the required amounts of constant boiling HCl, reagent grade KCl and boiled, nitrogen-saturated redistilled water. Distilled water was placed in the first saturator and the HCl-KCl solution in the others. Air was displaced from the sample tube and pipet with CO_2. CO_2 was bubbled through the saturators for about an hour to insure removal of all oxygen from the solution. About 0.4 gms. of $EuCl_2$ were

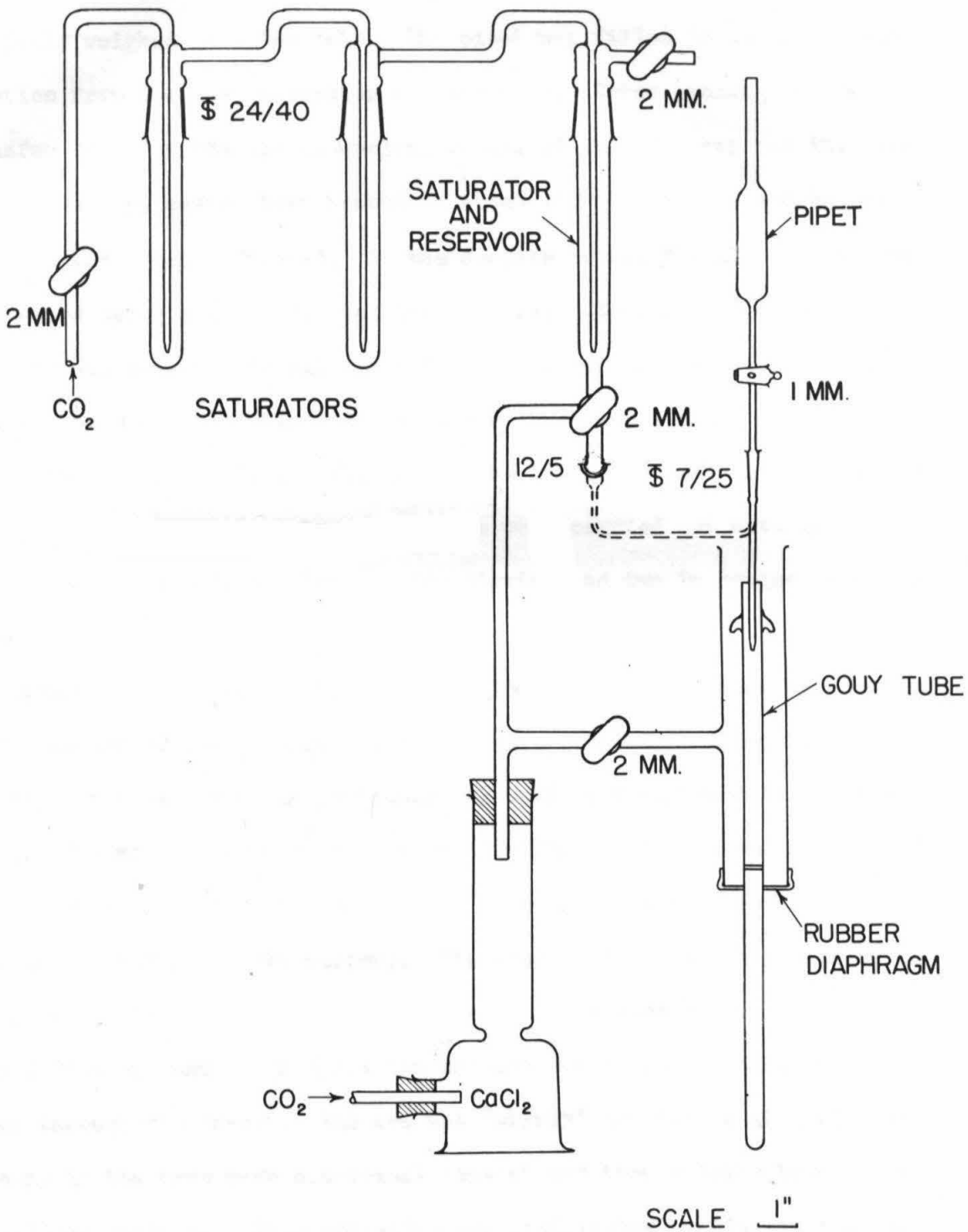

FIGURE I. GOUY TUBE FILLING APPARATUS.

carefully weighed into the tube. The pipet was filled to the mark with solution from the last saturator or reservoir. After exchanging the transfer tube for the tip extension, 12 ml. of solution was run into the tube. The cap, having been heated to about 150° C., was placed on the tube rim and a seal effected. As the density of the HCl-KCl solution was determined using a carefully calibrated Ostwald-Sprengel type pycnometer (22), it was possible to calculate from the weight of the tube and solution the volume of solution delivered and thus have a check on the pipet. After the wax had hardened solution of the $EuCl_2$ was effected by inverting and twirling the sample tube. Four runs were carried out with each HCl-KCl solution - two in clear tubes for irradiation and two in opaque tubes to follow the dark or thermal reaction, if any.

Prior to irradiation the susceptibility of the solutions was checked over a period of two or three days to insure attainment of equilibrium. The apparatus used for the photochemical work is diagrammed in Figures 2 and 3. The mercury arc, B, consisted of a "hairpin" of 1 cm. pyrex tubing with electrodes sealed into the end of each arm. It was about 40 cm. long and half-filled with mercury. The arcs were filled by attaching to a mercury still which in turn was connected to a good vacuum system (mercury diffusion pump). In operation the arc was cooled by circulating water through the jacket. The arc was "struck" by tilting it until the mercury in the arms made electrical contact and then quickly bringing to a vertical position. This operation was facilitated by hinging the end of the box, A, at the bottom. In nearly all cases the operating current was 6.0 amps. and the potential across the lamp 45-50 volts. After the rheostats in series with the arc had come to temperature a constant current

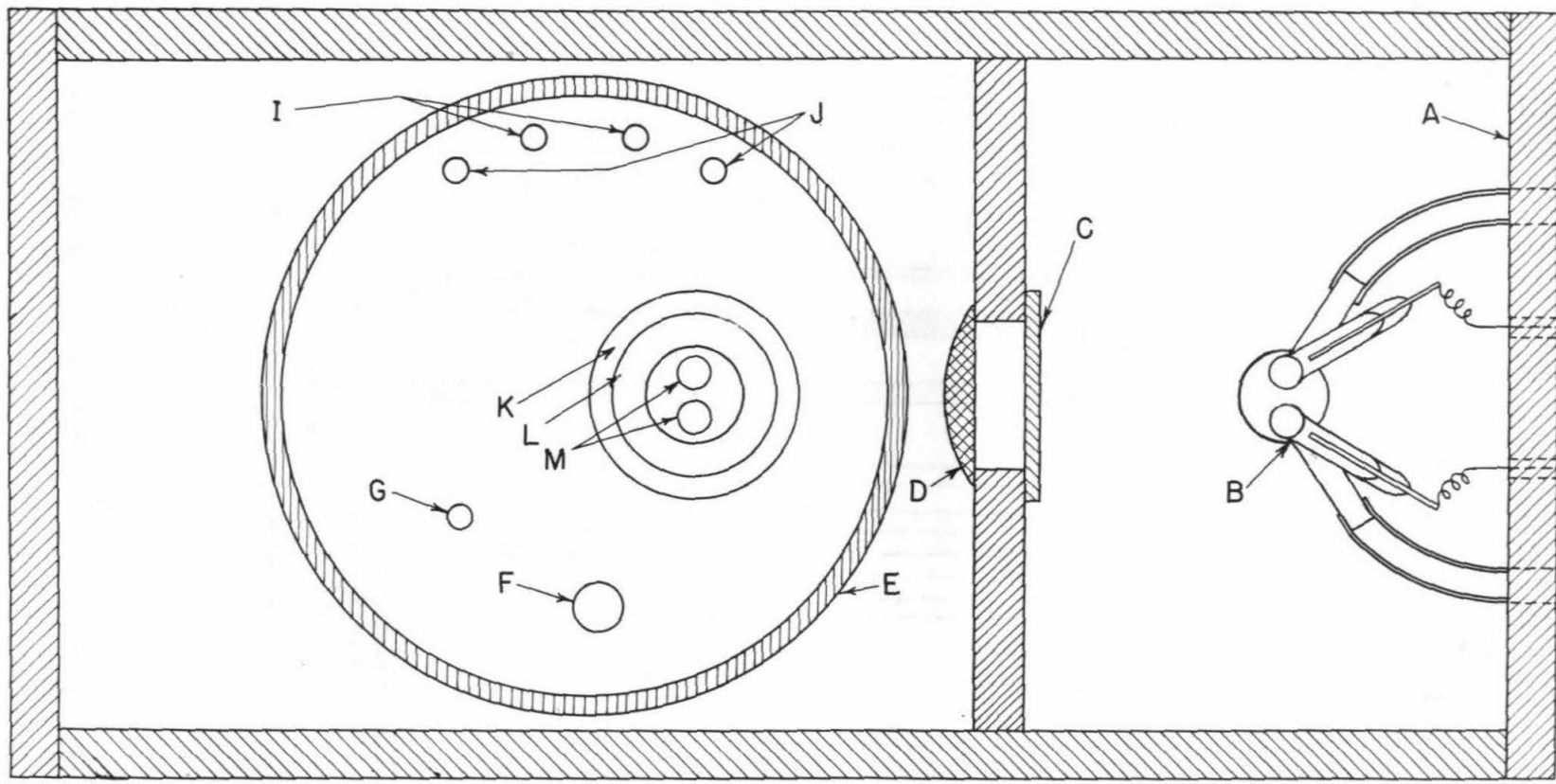

FIGURE 2.
PLAN VIEW OF PHOTOLYSIS APPARATUS.

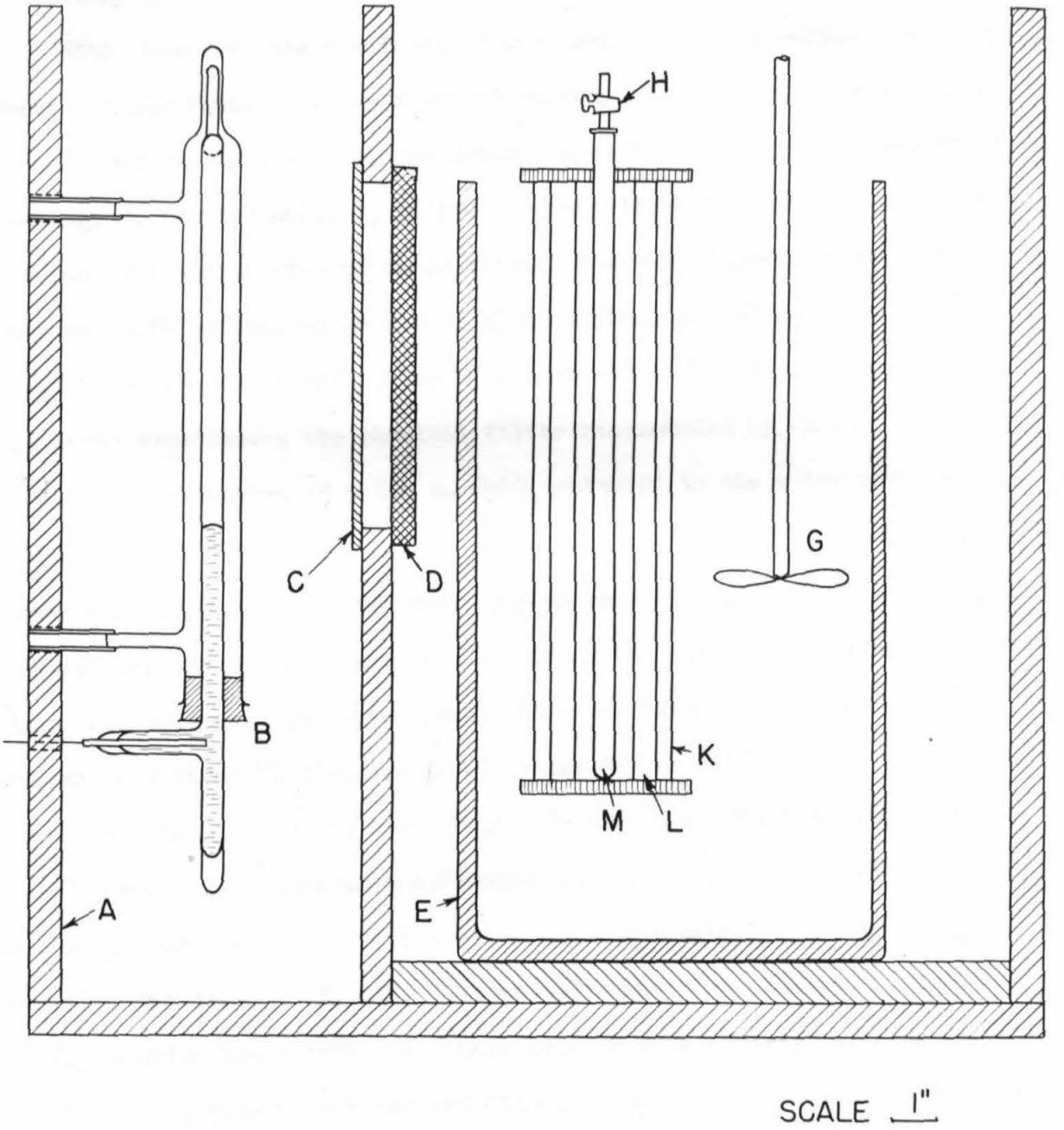

FIGURE 3.
SIDE VIEW OF PHOTOLYSIS APPARATUS

was easily maintained for periods of hours. Power was obtained from the laboratory generators.

With regard to the remainder of the photochemical apparatus the parts were: simple shutter, C; cylindrical condensing lens, D; 18" x 10" pyrex battery jar, E; Aminco thermoregulator, F; coil of 5/16" copper tubing for cooling, J; heating unit, I; stirrer, G; and light filtering cell, K and L. The last was constructed of three coaxially arranged pyrex tubes 36 cm. long and with outside diameters of 81 mm., 66mm. and 42 mm. The end pieces were grooved brass plates 4" square and 1/4" thick. For all of the later experiments the chemical filter recommended by Winther was used (23). This consisted of a 1.0 m. $CuSO_4$ solution in the outer annulus, K; and a solution of $CoCl_2$ in water (70 g. $CoCl_2 \cdot 6H_2O$ in 50 g. H_2O) in the inner annulus, L. The light path lengths were 0.5 cm. through annulus, K; and 1.0 cm. through annulus, L. The bath water circulated through the inner compartment. The above combination of filters served to limit the transmitted light to the line group around 365 mμ. Two series of experiments were carried out to check this. In the first the transmissions of the filtering solutions were determined using 1 cm. corex cells in the Beckman, Model D-U, Spectrophotometer. The transmission of the $CoCl_2$ solution was 31.9% at 365 mμ, 3.6% at 405 mμ and 0.4% at 435 mμ. The $CuSO_4$ solution transmitted all these wave lengths equally well but served to absorb any red or infrared radiation. Shorter wave lengths were effectively absorbed by the pyrex of the battery jar and filtering cell and by the crown glass of the condensing lens. The second experiment consisted in constructing a periscope arrangement whereby the light which actually reached the central tube of the cell could be directly observed with a

small Hilger Spectrograph. Quartz prisms were used in the periscope to avoid changing the spectral composition of the light. About twenty exposures varying from 2 sec. to 5 min. were made. From an inspection of the densities of the lines on the plates the following approximate ratio of intensities was obtained: 334: 365: 391: 405: 435 = 0.001: 10: 0.01: 1: 0.001. The results of the two sets of experiments are thus in agreement in showing that at least 90% of the light reaching the inner compartment of the cell consisted of the 365 mμ line group.

As can be seen from the figures the Gouy tubes, G, were placed in the central tube or chamber of the filtering cell. Generally one tube containing the reaction mixture and another containing a uranyl oxalate actinometer (24, 25) were placed side by side. A brass rack served to hold them securely in position. The actinometer solution was prepared, as recommended by Forbes and Heidt (25), by dissolving 0.01 mole of freshly precipitated uranyl oxalate and 0.05 mole of oxalic acid in 1 liter of distilled water. Other than this the procedures outlined by Leighton and Forbes (24) were used exclusively. The reaction involved in this actinometer is simply the decomposition of oxalic acid to water, carbon dioxide and carbon monoxide. The extent of decomposition is determined by titrating the solution with standard potassium permanganate. A volume of 12 ml. of actinometer was used and the whole amount titrated in beakers covered with opaque black paint. It was impossible to stir the actinometer and hence some error is introduced, as Leighton and Forbes quantum yields were determined with well stirred solutions. They report the error due to non-stirring to be about 20%. However, it is felt that it was probably smaller in these experiments as only 30% of the incident light is absorbed

by the actinometer. This point is further discussed below. The fraction of light absorbed by the actinometer was calculated for a cell of cylindrical cross section (I.D. = 0.422") assuming Lambert's law and using the absorption coefficient for light of wave length 365 mμ given by Leighton and Forbes. An outline of this calculation follows:

I_o = intensity of the uniform beam of incident light in energy/unit area.

$I(y)$ = intensity of light transmitted by the cell as a function of y, the distance from the plane through the center of the cell parallel to the beam.

a = radius of cell.

$2x$ = length of light path (coordinate system set up with origin at center of cell and x axis parallel to beam).

k = extinction coefficient ($\log k_{365} = 1.27$) in meters^{-1}.

L_o = total incident flux per unit length of cell = $2 a I_o$.

L = total emergent flux per unit length of cell = $2\int_o^a I(y)\, dy$.

$f = y/a$.

$I(y) = I_o 10^{-2xk}$ (Lambert's law).

$$L = 2I_o \int_o^a 10^{-2k\sqrt{a^2-y^2}}\, dy = 2aI_o \int_o^1 10^{-2ak\sqrt{1-f^2}}\, df.$$

$$L/L_o = \text{fraction transmitted} = \int_o^1 10^{-2ak\sqrt{1-f^2}}\, df.$$

For a = 0.211" and log k_{365} = 1.27 the value of this integral was determined by graphical methods to be 0.699. Hence the fraction of the incident light absorbed by the actinometer was 0.301. Using Leighton and Forbes' expressions for the total incident flux in time Δt one obtains:

$$L_o = \frac{6.025 \times 10^{23} \times m}{\phi \times (1 - L/L_o)},$$

where m is the number of moles of actinometer decomposed and ϕ is the quantum yield of the actinometer.

The absorption spectrum of solutions of $EuCl_2$ in 0.50 m. HCl was measured with the Beckman, Model D-U, Spectrophotometer. The results are given in Table 1.

TABLE 1

Absorption Spectrum of $EuCl_2$ in 0.50 m. HCl

Wave Length ($m\mu$)	[Eu(II)] (moles/liter)	Transmission (%)	D ($-\log_{10} T$)	$\alpha \left(\frac{D}{[Eu(II)]}\right)$
440	0.117	92.1		
435	0.117	88.9		
430	0.117	81.4	0.091	0.78
410	0.117	6.9	1.15	9.8
405	0.117	0.65	2.18	18.6
400	0.117	0		
380	0.117	0		
370	0.117	0		

TABLE 1

(Continued)

Wave Length ($m\mu$)	[Eu(II)] (moles/liter)	Transmission (%)	D ($-\log_{10} T$)	α $\left(\frac{D}{[Eu(II)]}\right)$
365	0.117	0		
360	0.117	0		
410	0.017	72	.144	8.5
380	0.017	0.93	2.03	122
365	0.0023	50.6	0.296	127

While the data are by no means extensive it is clear that the light of wave length 365$m\mu$ is very strongly absorbed by the $EuCl_2$ solutions. A calculation based on the assumption that Beer's law holds for solutions 0.1 m. in $EuCl_2$ gives greater than 99% absorption in 2 mm. The quantum efficiency calculations were based on total absorption of the incident light in the $EuCl_2$ solutions. Since the solutions contained only HCl, KCl, $EuCl_3$, $EuCl_2$ and H_2O, there were no species present, other than Eu(II) ion, which appreciably absorb light of the wave length used. With regard to $EuCl_3$ the absorption spectrum is given by Yost, Russell and Garner (26) and this was checked in preliminary experiments.

The use of the actinometer involves the assumption that the light intensity is uniform over the entire illuminated area. A number of preliminary experiments were run with two tubes containing the actinometer.

It was found that the light intensity varied by about 10% from one side of the inner compartment of the filtering cell to the other. However, periodic reversals of the positions of the tubes was found to give the same actinometer decomposition to within less than 1%. The reversal was easily accomplished by rotating the supporting rack through 180°. In practice eight to ten reversals were made during the usual ten hour irradiation.

In order to establish with certainty the susceptibilities of the two varieties of europium ion a number of additional experiments were carried out. Solutions of $EuCl_3$ and $Eu(NO_3)_3$ were made up and the susceptibility measured. These were analyzed for europium by precipitating it as the oxalate and igniting this to the oxide and weighing. Precautions were taken in the oxide weighings to prevent appreciable reaction with the carbon dioxide and water vapor in the air. The determination of the susceptibility of europium(II) ion was made by analyzing a number of the reaction mixtures for this ion - the photochemical reaction consuming about 10% of the Eu(II) in most cases. This procedure was necessary as it was not found possible to prepare solutions without some small initial oxidation of the $EuCl_2$. Analyses were carried out by opening the tubes in a "dry box" filled with CO_2. Using semi-micro pipets 0.5 ml. portions were transferred to 10 ml. flasks containing excess $Fe_2(SO_4)_3$ dissolved in 1.8 m. H_2SO_4. About 1 ml. of Zimmerman-Reinhardt "preventative" solution was added to inhibit the oxidation of the chloride ion present in the reaction mixture (27). The flasks were then removed from the "dry box" and the solutions titrated with 0.1 n. $KMnO_4$. Analyses were run in triplicate and blanks taken in all cases. The total europium content of

some of the reaction mixtures was determined as described above as a check on the amount of $EuCl_2$ added. All of the volumetric apparatus used in the semi-micro titration work was carefully calibrated.

Results and Discussion

A. Magnetic Susceptibilities of Europium(III) and Europium(II) Ions in Aqueous Solution

In calculating the susceptibilities of the europium ions in the solutions the validity of Wiedemann's additivity law was assumed (28). The expression for the law is

$$\chi_{obs.} = \sum_{i=1}^{n} \chi_i \cdot \omega_i ,$$

where $\chi_{obs.}$ is the observed susceptibility per gram, χ_i is the susceptibility of the i'th species and ω_i is the weight fraction of that species. If the subscript 1 designates the species of interest, then it can easily be shown that

$$\chi_{M_1} = \chi_1 \cdot M_1 = \frac{10^3}{m_1}\left\{\chi_{obs.} - 10^{-3} \sum_{i=2}^{n} \chi_{M_i} \cdot m_i\right\} ,$$

where χ_{M_i} is the molar susceptibility of the i'th species, m_i is the concentration of the i'th species in moles per liter and M_i is the molecular weight of the ion or molecule involved. The ionic diamagnetic susceptibilities which were used in the calculation are given in Table 2.

TABLE 2

Diamagnetic Susceptibilities at 25° C.

Substance	Molar Susceptibility $\chi_M \times 10^6$	Reference
H_2O	-12.97	(29)
HCl	-21.9	(30)
Cl^-	-25.1	(31)
NO_3^-	-18.5	(31)
K	-14.0	(31)
Na	-5.6	(31)
Eu(II) and Eu(III)	-30	(32)

The results of the measurements of the susceptibility of europium(III) ion in a magnetic field of about 9000 oersteds are presented in Table 3. Included with these are the results of other investigators and the pertinent theoretical value. The effective Bohr magneton numbers (μ_{eff}) are tabulated only as a convenient method of comparing results. It is clear that there is poor agreement between the experimental value of the moment of europium(III) ion and the theoretical value. In fact the difference is much larger than any error in the measurements. The explanation of this discrepancy is not evident, but some remarks can be made. Interaction between the europium(III) ion and some other constituent of the solution of sufficient magnitude to affect its magnetic properties is not likely. It is not to be expected theoretically (33) and is not seen

TABLE 3

Magnetic Susceptibility of Europium(III) Ion

Salt Used	[Eu(III)] (moles/liter)	[HCl] (moles/liter)	Force (gms.)	Density (gms./ml.)	Temp. (°C.)	Europium(III) $\chi_M \times 10^6$ (c.g.s./gm. ion)	Europium(III) μ_{eff} (Bohr magneton)	Reference
$EuCl_3$	0.994	0.497	0.1024	1.236	25.0 ± 0.1	4450	3.27	
$EuCl_3$	0.662	0.332	0.0612	1.156	25.0 ± 0.1	4400	3.26	
$EuCl_3$	0.331	0.166	0.0201	1.079	25.0 ± 0.1	4460	3.27	
$Eu(NO_3)_3$	0.815_1		0.0783	1.223	25.0 ± 0.1	4470	3.28	
$Eu(NO_3)_3$	0.431_5		0.0315	1.117	25.0 ± 0.1	4410	3.26	
$Eu(NO_3)_3$	0.368*		0.0247	1.315	25.0 ± 0.1	4480	3.28	
$Eu(NO_3)_3$	0.390**		0.0257	1.268	25.0 ± 0.1	4510	3.29	
					Average =	4450 ± 30	3.27	
$Eu(NO_3)_3$	0.196			1.093	23.5	4310	3.21	(34)
$Eu_2(SO_4)_3 \cdot 8H_2O$	Solid				20	4940	3.41	(35)
Eu(III)	Theoretical						3.40-3.51	(36)

* Solution 4.27 m. in $NaNO_3$.
** Solution 4.44 m. in NaCl.

in the above results, which cover a wide range of ionic strengths. Note can be taken here of the fact that such changes in the ionic environment do alter the absorption spectrum of europium(III) ion (37). Deviations from additivity of the diamagnetic constituents of the order of magnitude necessary to account for the discrepancy are also improbable. The possibility of some inadequacy in the theory remains.

Table 4 contains the measured values of the magnetic susceptibility of europium(II) ion, along with the results of other workers and the theoretical value. In calculating the susceptibility of the europium(II) ion the value obtained above for europium(III) was used exclusively. Clearly the agreement between the experimental and theoretical value for the isoelectronic gadolinium(III) ion is excellent (38, 39). This agreement is good evidence in support of the value obtained for europium(III) ion.

With regard to the errors in the magnetic measurements the following can be said. Temperature and density errors were negligible, being 0.1% or less. The error in the weighing was 0.2 mg. at a maximum; and this amounted to about 0.5%. In some cases the determination of the europium concentration could have been off by as much as 1%, but generally should have been considerably more accurate than this. Calibration of the tubes was repeated several times over the course of two years and the values obtained reproduced to at least 1%. In sum it is felt that the results obtained are reliable to 1% at the worst.

TABLE 4

Magnetic Susceptibility of Europium(II) Ion at 25° C.

[Eu(II)] (moles/liter)	[Eu(III)] (moles/liter)	Force (gms.)	Field (oersteds)	Ionic Strength of Solution*	$\chi_{obs.} \times 10^6$ (c.g.s./ml.)	Europium(III) $\chi_M \times 10^6$ (c.g.s./gm. ion)	Europium(III) μ_{eff} (Bohr magneton)	Reference
0.0688	0.0837	0.0367	9140	2.61	2.131	26020		
0.0732	0.0543	0.0374	9140	2.49	2.176	26320		
0.137	0.093	0.0869	9140	2.88	3.293	26520		
0.191	0.119	0.1310	9140	3.18	4.800	26070		
0.1225	0.0240	0.0752	9140	3.05	2.580**	26620		
0.1377	0.0088	0.0785	9140	2.01	2.857**	26100		
0.1380	0.0115	0.0760	9140	3.03	2.817**	26100		
					Average =	26250 ± 100	7.94	
$EuSO_4$							7.66	(40)
$Gd_2(SO_4)_3 \cdot 8H_2O$							8.11	(40)
Gd(III) Theoretical							7.94	(40)

* Solutions contained HCl and KCl.

** These values checked at 8680 oersteds.

B. The Photochemical Decomposition of Water by Europium(II) Ion

For the sake of clarity the data and calculations for one of the photochemical runs are presented below in some detail.

Experiment No. 16-b:

Sample tube No. 2 used.

Tube constant = 26660 at 9140 oersteds (13.00 amps.).

Tube constant = 23410 at 8680 oersteds (11.00 amps.).

The HCl-KCl solution was 0.50 m. in HCl and 1.05 m. in KCl.

Its density was 1.054 gms./ml. at 25.0° C.

0.3967 gms. $EuCl_2$ weighed into tube.

Total weight of solution in tube = 12.980 gms.

Normality of the $KMnO_4$ used in titrating the actinometer = 0.1194.

Blank actinometer titre = 11.73 ml.

Table 5 presents the magnetic susceptibility data and concentrations calculated therefrom. All measurements were made at 25.0 ± 0.2° C.; and the photochemical work was carried out at 25.3 ± 0.1° C. From the total weight of solution and the weight of $EuCl_2$, and assuming that the volumes of solution and $EuCl_2$ (d_4^{25} = 4.87 gm./ml.) (41) are additive, the total volume was calculated to be 12.03 ml. The molarity of the water in the final solution was determined by a direct calculation to be 52.8 and that of the europium to be 0.1480. In the table $K_{obs.}$ was calculated from the observed force on the tube and taking the diamagnetic susceptibility of laboratory air to be -0.029×10^{-6} c.g.s./ml. $\chi_{M(obs.)}$ is the average molar susceptibility of all the europium in the solution and was evaluated

TABLE 5

Experiment No. 16-b: Magnetic Susceptibility Data

Time (hrs.)	Force* (gms.)	Field (oersteds)	$K_{obs.} \times 10^6$ (c.g.s./ml.)	$\chi_{M(obs.)} \times 10^6$ (c.g.s./gm. ion)	$\frac{[Eu(II)]}{[Eu(II)]+[Eu(III)]}$	[Eu(II)] (moles/liter)	[Eu(III)] (moles/liter)
934.6	0.0796	9140	3.017	25.42	0.963	0.1425	0.0055
958.1	0.0794	9140	3.009	25.38	0.962	0.1424	0.0056
----------Irradiate here----------							
986.9	0.0768	9140	2.910	24.70	0.930	0.1376	0.0104
1102.8	0.0763	9140	2.891	24.59	0.926	0.1370	0.0110
1390.2	0.0757	9140	2.849	24.30	0.912	0.1350	0.0130
----------Irradiate here----------							
1422.7	0.0733	9140	2.779	23.81	0.889	0.1315	0.0165
1558.3	0.0732	9140	2.776	23.75	0.886	0.1311	0.0169
1558.3	0.0640	8680	2.761				

* Corrected for "pull" on empty tube in field.

by use of the equation on page 16 of this section. By taking the molar susceptibilities of europium(II) ion as 26250 x 10^{-6} c.g.s./gm. ion and that of europium(III) ion 4450 x 10^{-6} c.g.s./gm. ion, and assuming additivity, the fraction of europium in the bivalent state was calculated. From this the concentrations of the two species came directly, of course.

Two photochemical runs were made with this particular solution at the times indicated in Table 5. The data and calculated results for these runs are given in Table 6.

TABLE 6

Experiment 16-b: Photochemical Data*

(1) Change in Concentration of Eu(II)	(2) Molecules Eu(II) Oxidized x 10^{-19}	(3) Irradiation Time (Sec.)	(4) Actinometer Titre (ml.)	(5) Quanta Absorbed x 10^{-19}	(6) Quantum Yield
0.0038	2.76	41,600	11.17	13.6	0.20_4
0.0035	2.54	40,650	11.15	14.1	0.18_1
				Average =	0.19

* See Table 5 for other data on this experiment.

The first column came directly from the europium(II) concentrations listed in Table 5. This concentration change was converted into molecules oxidized in the usual manner. The number of quanta absorbed by the solution was calculated from the formula on page 13 of this section. It is repeated below with numerical values inserted.

$$L_o = \frac{6.025 \times 10^{23} \times (11.73 - \text{column } 4)}{0.492 \times 0.301}$$

In the denominator the second factor is the fraction of light absorbed by the actinometer, which was determined as described above. The first factor is the quantum yield of the uranyl oxalate actinometer for light of wave length 365 and for stirred solutions. The quantum yields (column 6) were calculated by dividing column 2 by column 4. They represent the total number of europium(II) ions oxidized per quantum absorbed.

Of the several sources of error in these measurements it is believed that the most important is that due to impracticability of stirring the solutions. Leighton and Forbes also give actinometer quantum efficiencies for unstirred solutions, and for the wave length used here it is about 20% smaller than that for stirred solutions. The error in the europium(II) quantum efficiencies is then in the direction of high values. It is believed unlikely that the error is as great as 20% in these experiments, however. Leighton and Forbes used cells at least three times longer than those used here and thus had much more nearly complete absorption of the light by the uranyl oxalate. This would give a gradient in the concentrations of the reactants much greater than with the shorter cells in which the light is only 30% absorbed. There is the possibility of a similar error involved with the europium(II) solutions. Here it could be more serious since the light is nearly completely absorbed within 2 mm. However, four considerations lead to the conclusion that the lack of stirring is not of great importance. In the first place, the light intensities were such that only a small fraction, about 2%, of the europium(II) ion was oxidized and thus the solution in the region of absorption was not significantly depleted in this species. Secondly,

since the limited data available indicate no marked dependence of the quantum yield on europium(II) ion concentration, and as neither of the reaction products absorb in the spectral region used, the small concentration gradients produced should have no effect on the quantum yield. In the third place, the evolution of gas was sufficient to produce a slow stream of bubbles which should have stirred the solution effectively. Finally, the periodic reversals of the positions of the tubes, causing first one side to be irradiated and then the other, compensated in part for the lack of stirring.

The light filtering cell was constructed with a large hole in the bottom of the inner compartment, which contained the reaction tubes. This permitted thermostat water to surround the tubes completely, greatly reducing the reflection of light from the walls. However, because of the cylindrical shape of the tubes the reflection must have been considerable for light incident at the glancing angle. Any error caused by this would, however, cancel as the actinometer tube and reaction tube were identical. This argument applies to the incident light only. Since the actinometer absorbed only 30% of the light there was some reflection from the rear walls of the tube, which was not present in the europium(II) solutions. Such reflection would give high values for the incident light intensity and thus low values for the europium(II) quantum yield. The magnitude of this error should not be greater than 1 or 2%. Due to the small amount of actinometer decomposed the error in its determination amounted to 3 to 4% in the most unfavorable cases. The other significant errors have been previously discussed. In summary, it is believed that the values of the quantum efficiencies obtained are limited in their accuracy to the extent

of at least 10%.

Before this investigation was put aside to pursue the problem of "Age Determination by Carbon-14 Content", described in Part IV of this thesis, a number of experiments were carried out. The results of these and the data concerning the experimental conditions are given in Table 7. The temperature of the bath was maintained at 25.3 ± 0.1° C. in all experiments. Those experiments marked with an asterisk were done with a 1.0 m. $CuSO_4$ filter only. In the calculations for these cases the quantum efficiency and absorption coefficient of the actinometer were approximated by taking the averages of the values for the 365 mμ, 405 mμ and 435 mμ line groups. A correction factor of 0.70 was applied to the flux so obtained to account for the fact that europium(II) solutions do not absorb the 435 mμ lines. This factor was derived from the relative intensities of the various lines given by Plotnikow (42).

In the preliminary experiments previously mentioned, solutions 0.3 m. in $EuCl_2$ and 0.25 m. in HCl showed no appreciable thermal reaction at temperatures ranging from 25° C. to 70° C. The thermal reaction at room temperature was extensively studied, two sources of data being provided. The first derives from the fact that the susceptibility of the reaction mixtures was determined before and after each irradiation period. During the interim periods, which sometimes amounted to several days, the tubes were kept in a light-tight container. Thus the measurements used for the photochemical reaction also gave an indication of the extent of dark reaction. The second source of data is more direct in that two tubes were coated with an opaque black paint and filled with reaction mixtures just as were the clear tubes. These opaque tubes were kept in a

TABLE 7

Photochemical Decomposition of Water by Europium(II) Ion

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	[HCl] (moles/liter)	[KCl] (moles/liter)	Molecules Eu(II) Oxidized x 10^{-19}	Quanta Absorbed x 10^{-19}	Quantum Yield
12*	0.2959	0.2792	0.023	1.89		12.3	43.4	0.28
12*	0.2792	0.2629	0.039	1.88		12.1	45.9	0.26
12*	0.2629	0.2558	0.051	1.87		5.26	17.7	0.30
12*	0.2558	0.2486	0.058	1.85		5.32	19.7	0.27
12*	0.2486	0.2386	0.067	1.84		7.40	24.5	0.30
12*	0.2386	0.2307	0.076	1.82		5.85	20.4	0.29
12*	0.2307	0.2242	0.083	1.81		4.81	19.7	0.24
12*	0.2233	0.2086	0.094	1.80		10.9	40.4	0.27
12*	0.2070	0.1996	0.107	1.79		5.48	19.4	0.28
12*	0.1996	0.1921	0.114	1.78		5.56	24.5	0.23
							Average =	0.27
14-a*	0.1461	0.1397	0.007	0.49	0.05	4.60	38.9	0.12

* 1.0 cm. $CuSO_4$ filter only. See page 26.

TABLE 7

(Continued)

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	[HCl] (moles/liter)	[KCl] (moles/liter)	Molecules Eu(II) Oxidized x 10^{-19}	Quanta Absorbed x 10^{-19}	Quantum Yield
14-a*	0.1397	0.1318	0.015	0.48	0.05	5.69	47.5	0.12
14-a*	0.1318	0.1265	0.021	0.48	0.05	3.82	32.5	0.12
14-a*	0.1265	0.1219	0.026	0.47	0.05	3.31	30.6	0.11
14-a*	0.1219	0.1172	0.031	0.47	0.05	3.38	31.8	0.11
14-a*	0.1172	0.1133	0.035	0.46	0.05	2.81	30.0	0.093
14-a*	0.1133	0.1095	0.039	0.46	0.05	2.74	27.8	0.10
14-a*	0.1095	0.1050	0.043	0.46	0.05	3.24	34.3	0.094
14-a	0.1050	0.1034	0.046	0.45	0.05	1.15	5.74	0.20
14-b*	0.1451	0.1390	0.007	0.49	0.05	4.39	31.5	0.14
14-b*	0.1390	0.1350	0.013	0.49	0.05	2.88	26.8	0.11
14-b*	0.1350	0.1305	0.017	0.48	0.05	3.24	30.8	0.11

* 1.0 cm. $CuSO_4$ filter only. See page 26.

TABLE 7

(Continued)

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	[HCl] (moles/liter)	[KCl] (moles/liter)	Molecules Eu(II) Oxidized x 10^{-19}	Quanta Absorbed x 10^{-19}	Quantum Yield
14-b*	0.1305	0.1258	0.022	0.48	0.05	3.38	30.7	0.11
14-b*	0.1258	0.1215	0.026	0.47	0.05	3.09	28.0	0.11
14-b	0.1215	0.1188	0.030	0.47	0.05	1.94	8.74	0.22
14-b	0.1188	0.1173	0.032	0.47	0.05	1.08	8.50	0.13
14-b	0.1173	0.1143	0.034	0.47	0.05	2.16	16.8	0.13
						Average of last three	=	0.15
14-c*	0.1369	0.1320	0.019	0.48	0.05	3.50	27.2	0.13
14-c*	0.1320	0.1269	0.023	0.48	0.05	3.64	31.0	0.12
14-c	0.1269	0.1234	0.028	0.47	0.05	2.50	16.3	0.15
14-c	0.1234	0.1198	0.032	0.47	0.05	2.57	14.9	0.17
						Average of last two	=	0.16

* 1.0 cm. $CuSO_4$ filter only. See page 26.

TABLE 7

(Continued)

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	[HCl] (moles/liter)	[KCl] (moles/liter)	Molecules Eu(II) Oxidized x 10-19	Quanta Absorbed x 10-19	Quantum Yield
16-b	0.1424	0.1376	0.008	0.49	1.05	2.75	13.6	0.20
16-b	0.1350	0.1315	0.015	0.48	1.05	2.54	14.1	0.18
							Average =	0.19
17-a	0.1425	0.1393	0.007	0.49	2.05	2.33	8.26	0.28
17-a	0.1393	0.1363	0.011	0.49	2.05	2.18	10.7	0.20
17-a	0.1363	0.1304	0.015	0.48	2.05	4.29	19.4	0.22
17-a	0.1304	0.1241	0.021	0.48	2.05	4.58	25.0	0.18
							Average =	0.21
17-b	0.1348	0.1309	0.013	0.49	2.05	2.88	13.4	0.21
17-b	0.1301	0.1255	0.019	0.48	2.05	3.40	16.3	0.21
							Average =	0.21

TABLE 7

(Continued)

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	[HCl] (moles/liter)	[KCl] (moles/liter)	Molecules Eu(II) Oxidized x 10-19	Quanta Absorbed x 10-19	Quantum Yield
20-a	0.1387	0.1351	0.012	0.99	1.55	2.65	10.94	0.24
20-a	0.1351	0.1290	0.017	0.98	1.55	4.49	15.1	0.30
20-a	0.1290	0.1227	0.023	0.98	1.55	4.64	15.8	0.29
20-a	0.1227	0.1172	0.029	0.97	1.55	4.05	14.8	0.27
20-a	0.1172	0.1111	0.035	0.96	1.55	4.49	16.8	0.27
							Average =	0.27
20-b	0.1432	0.1402	0.003	0.99	1.55	2.20	10.94	0.20
20-b	0.1402	0.1347	0.007	0.98	1.55	4.04	11.9	0.34
20-b	0.1347	0.1296	0.012	0.98	1.55	3.74	13.6	0.27_5
20-b	0.1296	0.1248	0.018	0.97	1.55	3.52	13.4	0.26
							Average =	0.27

thermostated bath at 25.0± 0.1° C. for long periods of time. They were removed every few days and the susceptibility determined. Table 8 presents the results of the experiments using the opaque tubes and some of the results from the clear tubes. The latter are marked with an asterisk. The temperature in these cases was that of the room and varied several degrees about 25° C. It is evident that the thermal rate is two to three orders of magnitude smaller than the photochemical rate at the light intensities used. For this reason no correction for the thermal reaction was applied to the photochemical yields. On several occasions it was noted that the thermal rate was much increased when solid particles were present in the solutions. Invariably the clearest solutions decomposed most slowly. Charcoal and platinized platinium induced a rapid decomposition - evidenced by a vigorous evolution of hydrogen. In all probability the dark reaction is primarily a surface effect caused by a lowering of the hydrogen overvoltage at the surface. R. A. Cooley reports the complete thermal decomposition in 80 hours in 3.82 m. HCl and reaction to the extent of 50% in 160 hours in 2.10 m. HCl (43). However, he does not give any indication as to whether light was entirely excluded or whether the solutions were entirely free of dust or other solid particles.

The literature contains reports of two investigations of quite similar systems. One is the photochemical reduction of water by iron(II) ion (44) and the other the same reaction with chromium(II) ion (45, 46). The results of these investigations are tabulated in Table 9.

TABLE 8

Thermal Decomposition of Europium(II) Chloride Solutions at 25° C.

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	Reaction Time (hrs.)	[HCl] (moles/liter)	[KCl] (moles/liter)	$\frac{d[Eu(II)]}{dt}$ (moles/liter/hr.)
9	0.0767	0.0742	0.069	140.8	0.41	1.50	1.8×10^{-5}
9	0.0677	0.0669	0.077	118.0	0.40	1.50	0.7×10^{-5}
10	0.1115	0.0944	0.024	165.8	0.97	1.00	10.3×10^{-5}
11	0.224	0.138	0.049	1028	0.95	1.00	8.3×10^{-5}
14-a*	0.1265	0.1265	0.024	68.6	0.48	0.05	
14-b*	0.1258	0.1258	0.024	139.6	0.48	0.05	
14-c*	0.1278	0.1269	0.026	259.7	0.48	0.05	0.4×10^{-5}
15-a	0.1286	0.1279	0.020	723.8	0.49	0.05	0.1×10^{-5}
16-b*	0.1376	0.1350	0.012	403.3	0.48	1.05	0.6×10^{-5}
17-a*	0.1430	0.1425	0.0055	165.0	0.49	2.05	0.3×10^{-5}
18-a	0.1405	0.1369	0.008	623.8	0.49	1.05	0.6×10^{-5}
19-a	0.1425	0.1352	0.011	625.2	0.49	2.05	1.2×10^{-5}

* See page 32.

TABLE 8

(Continued)

Exp't. No.	Initial [Eu(II)] (moles/liter)	Final [Eu(II)] (moles/liter)	Mean [Eu(III)] (moles/liter)	Reaction Time (hrs.)	[HCl] (moles/liter)	[KCl] (moles/liter)	$\frac{d[Eu(II)]}{dt}$ (moles/liter/hr.)
21-a	0.1401	0.1398	0.006	211.5	0.99	1.55	0.14×10^{-5}
21-a	0.1398	0.1360	0.009	3840	0.98	1.55	0.1×10^{-5}

TABLE 9

Photochemical Reduction of Water by

Iron(II) and Chromium(II) Ions

Ion	[M(II)] (moles/liter)	[H_2SO_4] (moles/liter)	Quantum Yield	Corrected Quantum Yield	Reference
Fe(II)	0.5	0.1	0.030	0.010	(44)
Fe(II)	0.5	0.25	0.020	0.007	(44)
Fe(II)	0.4	0.25	0.033	0.011	(44)
Fe(II)	0.5	0.25	0.047	0.016	(44)
Cr(II)	1.0	2.0	0.41	0.14	(46)
Cr(II)	1.0	0.5	0.35	0.12	(46)
Cr(II)	1.0	0.25	0.33	0.11	(46)
Cr(II)	1.0	0.05	0.33	0.11	(46)
Cr(II)	1.0	0	0.28	0.09	(46)

In both of these studies a quartz jacketed mercury arc was used as a light source and monochloroacetic acid as an actinometer. Both assumed a quantum yield for this actinometer of 1.0, while recent work has shown it to be nearer 0.32 (47, 48). Dain and Liberson make a note of this error but apply no correction for it. The quantum yields tabulated under "corrected quantum yield" in Table 9 are corrected by a factor of one-third to take account of this. It is clear that the results are quite comparable to those obtained here for Eu(II) ion.

At this point it is appropriate to consider this type of reaction in

detail and review the pertinent experimental facts. The first point to be emphasized is that the quantum efficiencies are all significantly less than one. A second fact of prime importance is that, except in the iron case, the bivalent ions are the only absorbing species in the solution. This statement is true for the iron(II) reaction only for solutions in which the iron(III) concentration is very small. In the europium and chromium cases no inhibiting effect of the tripositive ion is evident. Once again the iron reaction is exceptional in that iron(III) ion greatly inhibits the reaction - an effect over and above that due to absorption of the light by iron(III) ion. A definite increase in quantum yield with increasing acid concentration exists in the chromium and europium reactions.* Weiss' data are not extensive enough to reveal such a trend but at least they are not in contradiction to it. The chromium(II) quantum yield was found to be independent of temperature from 17° C. to 50° C. The thermal reaction is not significant over a considerable range of temperature. There appears to be some increase in quantum efficiency of the Eu(II) reaction with increase in ionic strength of the solution. No search was made for this effect by Dain and Liberson, and hence it is included in the increase in quantum yield with increasing H_2SO_4 concentration, which they report. The data for the europium(II) reaction show no significant dependence of the quantum yield on the concentration of Eu(II) ion over a range of from about 0.1 m. to 0.15 m.

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* The quantum yield at HCl = 2.0 m. (Exp't. No. 12) can be corrected by a factor of 1.3. This factor was derived from the ratio of the quantum yields determined with $CuSO_4$ and with $CuSO_4$-$CoCl_2$ filters (Exp'ts. No. 14-b and 14-c). Application of this factor increases the 2.0 m. quantum yield to 0.35, to lend support to the statement above.

Weiss suggests the following mechanism for this general type of reaction (44, 49). The primary process is

$$M(II) \cdot H_2O + h\nu = M(II)^* \cdot H_2O$$

$$M(II)^* \cdot H_2O = M(III)_{aq} + OH^-_{aq} + H$$

followed by

$$2H = H_2.$$

The reverse reaction is the reduction of the M(III) ion by the hydrogen atom, which we have seen does not occur in the europium and chromium reactions. The low quantum yield implies a high probability of the degradation of the energy of the activated M(II) ion through collisions with the water molecules. The primary process postulated by Weiss is almost certainly correct, as the ion is surrounded by a hydration layer of water molecules and the most probable way for it to give up an electron is to transfer it to a water molecule, with consequent dissociation of the latter into a hydroxyl ion and a hydrogen atom. The second step seems open to some question, however. The hydrogen atoms will be present at extremely low concentration and hence the probability of their combining to form molecular hydrogen will be very small. They are more likely to react with substances present at "ordinary" concentrations, if any such reactions are possible. In the Fe(II) case such a reaction is the reduction of Fe(III); and this probably accounts for the ten-fold lower quantum yield for this reaction. Another possibility has been suggested by Weiss, namely, the formation of hydrogen molecule ion (50). Weiss states that he has evidence indicating the presence of this ion in strongly acid solutions. In view of this, and taking account of the fact that the hydrogen molecule ion should possess oxidizing properties, the

following mechanism is proposed:

$$M(II) \cdot H_2O + h\nu = M(II)^* \cdot H_2O$$

$$M(II)^* \cdot H_2O = M(III)_{aq} + OH^-_{aq} + H$$

$$H + H^+_{aq} = H^+_{2aq}$$

$$M(II)_{aq} + H^+_{2aq} = M(III)_{aq} + H_2$$

It is not necessary to assume that the hydrogen molecule ion exists as such for any considerable period of time. The hydrogen atom, once escaping from the scene of the primary reaction and wandering through the solution, will frequently approach a hydrogen ion. If the hydrogen molecule ion exists for even a short time after one of these collisions then the possibility of reaction with an M(II) ion is considerable as these are present in large amount. In effect the hydrogen atom catalyzes the oxidation of M(II) by hydrogen ion - a change which, for Eu(II) and Cr(II), occurs with a large decrease of free energy. The fact that the oxidation of iron(II) ion does not have such a thermodynamic tendency means that in all probability it will not be oxidized by the hydrogen molecule ion. In fact, as we have seen, the iron(III) is reduced by the H atom (or H_2^+ ion).

The overall reaction implied by the above mechanism is

$$2Eu(II)_{aq} + 2H^+_{aq} = 2Eu(III)_{aq} + H_2 \qquad -\Delta F = 0.86 \text{ e.v.}$$

$$H_2O = H^+_{aq} + OH^-_{aq} \qquad -\Delta F = -0.83 \text{ e.v.}$$

$$2Eu(II)_{aq} + H_2O + H^+_{aq} = 2Eu(III)_{aq} + OH^-_{aq} + H_2 \qquad -\Delta F = 0.03 \text{ e.v.}$$

The overall reaction then has some tendency to proceed. It should be noted here that the interpretation of the quantum efficiencies is affected by the assumed mechanism. These efficiencies are reported as ions of Eu(II) oxidized per quantum absorbed. As each quantum results in the

oxidation of two such ions the "effective" quantum efficiencies are only one-half as great.

That the proposed mechanism, and also that of J. Weiss, are in accord with the experimentally observed hydrogen ion dependence can be seen from the following considerations. The Franck-Rabinowitch principle attributes the marked reduction in quantum yields usually observed on going from a gaseous system to a condensed system to the high probability of recombination of the dissociation products before they can escape from the "solvent cage", during which time they are near neighbors (51). In the above systems an increase in the hydrogen ion concentration should increase the ease with which the OH^- ion and the H atom can escape from the cage by increasing the chance that these can react to form the stable products H_2O and H_2^+.

The energetics of the primary reaction can be approached in two ways. Weiss gives the following equation for the energy required to transfer an electron to a water molecule in the hydration layer of the M(II) ion,

$$h\nu = D_{H_2O} - I_{M(II)} + E_{OH} + X$$

$$X = -H_{M(II)} + H_{OH^-} + H_{M(III)} \quad ,$$

where D_{H_2O} is the dissociation energy of the water molecule into H and OH, $I_{M(II)}$ is the ionization potential of the M(II) ion, E_{OH} is the electron affinity of the OH radical and H_k is the hydration energy of the species indicated. This approach is not very fruitful as the hydration energies are not known. Weiss suggests another treatment thus:

$$M(II)_{aq} + H^{+}_{aq} = M(III)_{aq} + \tfrac{1}{2}H_2 + E_1$$

$$\tfrac{1}{2}H_2 = H \qquad -2.2 \text{ e.v.}$$

$$H_2O = H^{+}_{aq} + OH^{-}_{aq} \qquad -0.8 \text{ e.v.}$$

$$M(II)_{aq} + H_2O = M(III)_{aq} + OH^{-}_{aq} + H + E_1 \qquad -3.0 \text{ e.v.}$$

E_1 is simply the oxidation-reduction potential for the given system. For the europium(II) reaction the energy required is 2.6 e.v. The energy of radiation of wave length 365 mμ is about 3.4 e.v. and is therefore more than sufficient. The energy of radiation corresponding to the long wave absorption edge (440 mμ) of europium(II) ion is 2.9 e.v. and hence it is predicted that this reaction will take place up to that limit.

It is evident that much work remains to be done with reactions of this type. The dependence of the quantum yield on $[H^{+}]$ should be further studied, as well as the possible dependence on $[Eu(II)]$.

In addition to the systems discussed above the titanium(II) reaction has been suggested (49). Another ion which should photochemically reduce water is vanadium(II). An investigation of the quantum yields for these last two systems would be very interesting as their absorption spectra should lie toward longer wave lengths. Most important of all a search should be made for conditions under which the quantum efficiencies can be increased toward their theoretical limit. The effect of a radical change in solvent, such as might be caused by addition of methanol, should also be investigated.

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PART II

THE MAGNETIC SUSCEPTIBILITY OF EUROPIUM AND SAMARIUM AMALGAMS

Introduction

The difficulties encountered in preparing the rare-earth metals have seriously hampered the investigation of the physical and chemical properties of these substances (1). By far the most extensive piece of work is that of Klemm and Bommer (2). These investigators prepared the metals by reducing the anhydrous trichlorides with the stoichiometric amount of potassium. The resulting mixture of rare-earth metal plus three moles of KCl proved quite suitable for the determination of the structures and the magnetic susceptibilities of the metals.

The purpose of the present investigation was to determine the magnetic susceptibilities of samarium and europium in dilute amalgams. While the literature contains many references to studies of the magnetochemical properties of amalgams (3), particularly those of the alkali metals, it appears that this approach to the study of the rare-earth metals has been neglected. Preparation of the amalgams was effected by reducing the rare-earth acetates in solution with sodium amalgam (4). After washing with water the liquid amalgams were introduced into tubes and the susceptibility determined by the Gouy method (5, 6).

Experimental

The Gouy balance used is described in Part I of this thesis. The

sample tubes were of the usual partition type. They were constructed from 8 mm. O.D. pyrex tubing and fitted with caps made from standard taper joints, size 12/18. When filled to the reference mark the tubes contained approximately 4.5 ml. of amalgam. Nickel chloride solution was used for calibration.

The origin and purity of the europium used in this research has been discussed in Part I of this thesis. The samarium was obtained from Research Chemicals, Inc.*, and was reported by them to be greater than 99% Sm_2O_3, the maximum amounts of impurities being: 0.25% Gd, 0.1% Eu and 0.1% other rare-earths. A determination of the susceptibility of samarium(III) chloride in dilute HCl solution showed no appreciable paramagnetic impurity. Redistilled mercury as obtained from the stockroom was used throughout. As far as possible a single batch was employed for each set of determinations. The magnetic susceptibility of the mercury was determined in order to establish its purity as regards paramagnetic or ferromagnetic substances. As can be seen from Table 1 excellent agreement was obtained with the latest values from the literature.

TABLE 1

Magnetic Susceptibility of Mercury

Investigators	Temp. °C.	$\chi_{Hg} \times 10^6$ c.g.s./gm.	Reference
L. F. Bates and C. J. W. Baker	18.5	-0.1681	(7)

* This concern, located at 831 North Lake Street, Burbank, California, offers for sale an excellent selection of rare-earth materials at moderate prices.

TABLE 1

(Continued)

Investigators	Temp. °C.	$\chi_{Hg} \times 10^6$ c.g.s./gm.	Reference
S. R. Rao and S. Aravamuthachari	"room temp."	-0.1660	(8)
D. L. Douglas	25	-0.166 ± .001*	

* Average of three determinations.

In a typical amalgam preparation 2.0 gms. of samarium acetate were dissolved in 13 ml. of water in a 60 ml. separatory funnel and 0.5 ml. of glacial acetic acid was added. Three portions of dilute sodium amalgam were prepared by dissolving 8 gms. of a previously prepared stock of 2.8% sodium amalgam (9) in about 65 gms. of redistilled mercury. One portion was added with gentle shaking to the acetate solution. A vigorous evolution of hydrogen resulted, and the gas was released by inverting the funnel and opening the stopcock. After about 20 sec. the solution took on a deep red color which lasted 10-30 sec. In the case of europium amalgam the color was light green and persisted throughout the treatment. When the evolution of hydrogen decreased markedly - after 1-2 min. of reaction - the amalgam was run into a 125 ml. separatory funnel containing 50 ml. of distilled water. The treatment was repeated with the other portions, 0.5 ml. of acetic acid being added prior to addition of each. The three "extracts" were combined in the large separatory funnel and gently shaken to attain complete mixing and removal of any unreacted sodium. The samarium amalgam reacts only slowly with water and europium

amalgam virtually not at all. After washing and mixing the amalgam was run into the reservoir of the filling apparatus shown in Figure 1. Air was pumped off and replaced by nitrogen dried over P_2O_5. This brief contact with air was sufficient for the formation of a dark scum on the samarium amalgam, but not on the europium*. Filling of the Gouy tubes was accomplished by evacuating them and allowing the amalgam to run into the tubes to the calibration mark. Dry nitrogen was admitted above the amalgam, the tube removed and the cap put on at once. The susceptibility was then measured with the Gouy balance - usually at room temperature.

One attempt was made to prepare europium amalgam by the electrolytic method of Jukkola, Audrieth and Hopkins (10). The cell is diagrammed in Figure 2. In this experiment 210 gms. of redistilled mercury were placed in the cell. Over this was put a solution of 4.18 gms. of anhydrous $EuCl_3$ (see Part I for preparation) in 20 ml. of absolute alcohol and 3.5 ml. of reagent grade chloroform. This was electrolyzed at 5-10 ma./sq.cm. for about two hours. At the end of this period a colorless and odorless gas, probably oxygen, was being evolved vigorously from the carbon anode and a crust had formed on the mercury. The amalgam was then washed with distilled water and transferred to the reservoir. The low yield is ascribed to insufficient drying of the reagents.

In all cases the amalgams were analyzed by treating a weighed portion with 6N HCl. On adding the acid a vigorous evolution of hydrogen ensued; and gentle heating and stirring sufficed to effect complete extraction of the rare-earth metal within a few minutes. This was checked by

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* In one case air was drawn through the samarium amalgam due to a leak in the lower stopcock. A copious scum formed but no great amount of samarium was consumed.

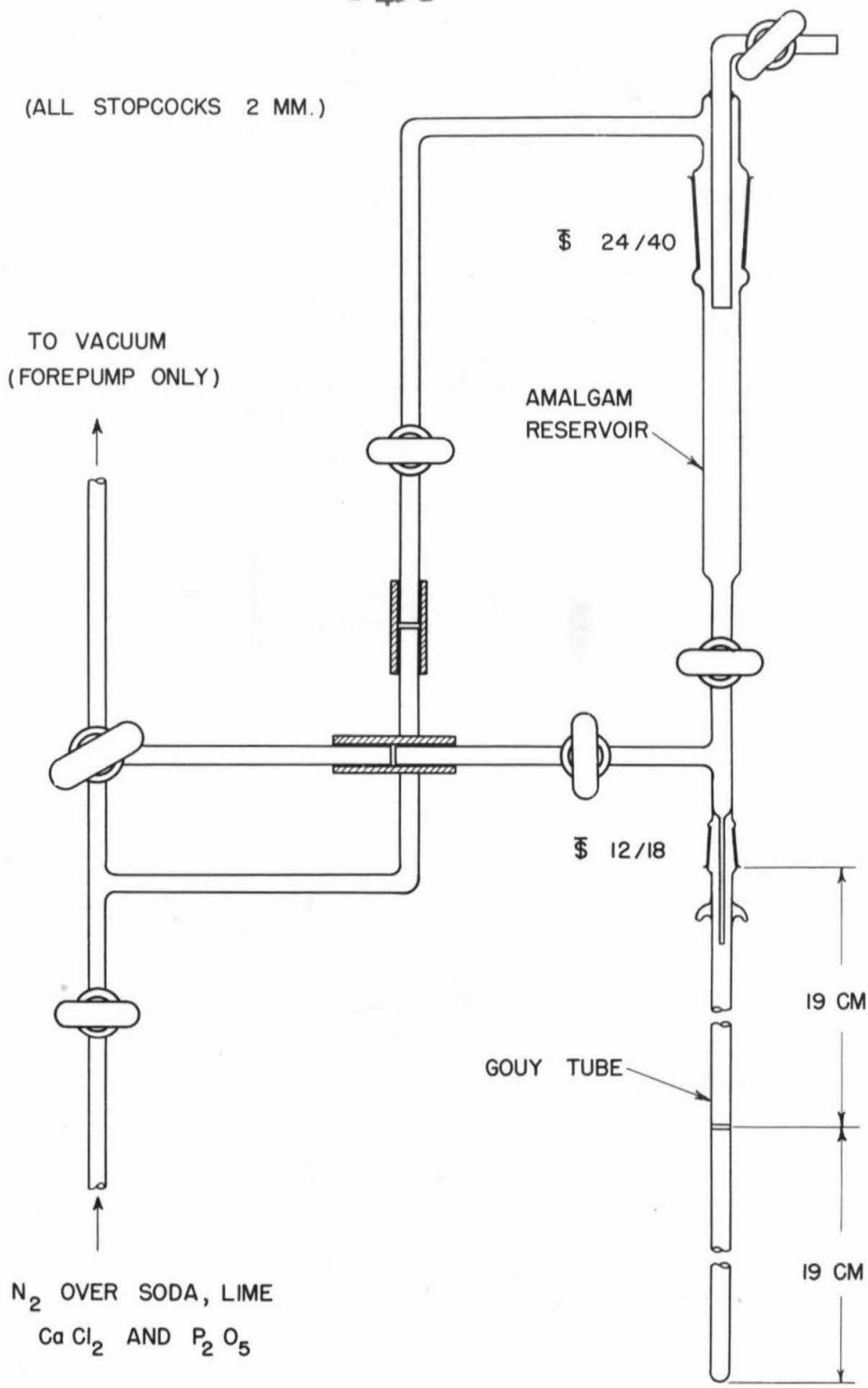

FIGURE 1. GOUY TUBE FILLING APPARATUS

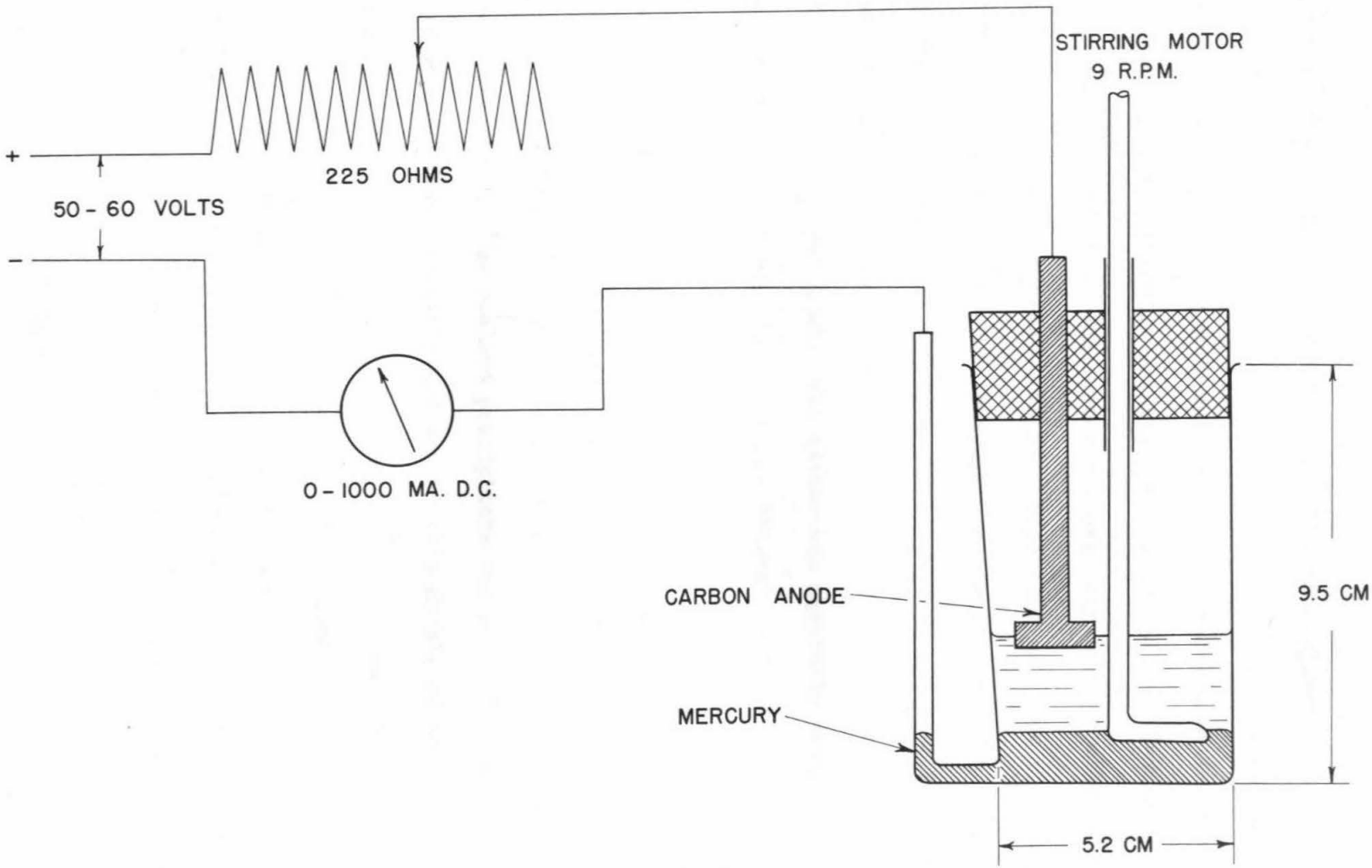

FIGURE 2. ELECTROLYSIS APPARATUS.

allowing the mercury, after separation from the extracting solution, to stand in contact with more 6N HCl for several days. This second "extract" was tested for rare-earth and none was found. After dilution to about 50 ml., the rare-earth chloride solution was saturated with H_2S and the resulting HgS filtered off. The rare-earth was then precipitated as the hydroxide by addition of excess 6N NH_4OH. Digestion on a hot plate at about 80° C. for an hour served to coagulate somewhat the difficultly handled hydroxide precipitate. This was collected on a filter paper and after washing with distilled water was dissolved in the minimum amount of 6N HNO_3 - usually about 1 ml. The filter was carefully washed and the combined nitrate solution and washings diluted to 50 ml. and heated to boiling. Hot oxalic acid solution (ca. 0.05 gms. $H_2C_2O_4$ per ml.) was added dropwise with stirring until precipitation was complete, and then 5-10 ml. excess was added. The mixture was digested either on a hot plate or in a water bath at 100° C. for 1-2 hours to consolidate the precipitate (11). The oxalate precipitate was collected in an ignited and weighed Gooch crucible and washed with 20 ml. of hot water. After drying for one hour at 110° C. the precipitate was ignited to constant weight at 850° C. in an electric muffle furnace. The crucible containing the resulting oxide was cooled in a desiccator and weighed quickly to prevent appreciable reaction of the oxide with water vapor and carbon dioxide in the air. Analyses generally were done in duplicate.

Results and Discussion

In calculating the susceptibilities of the rare-earth component of the amalgams the validity of Wiedemann's law was assumed throughout (12).

While it is by no means rigorously correct, the law appears to hold very well for the case of the rare-earths, where the interaction between neighboring atoms is too weak to perturb the 4f electron levels. For the general case of r components the expression is

$$\chi_{obs.} = \sum_{i=1}^{r} \chi_i \cdot w_i ,$$

where $\chi_{obs.}$ is the observed susceptibility per gram, χ_i is the specific susceptibility of the i'th component and w_i the weight fraction of that component. Measurements were made at two field strengths to detect any field strength dependence. In all cases the susceptibility values were found to be independent of field strength, indicating the absence of appreciable ferromagnetic impurities.

The principal error in the measurements is considered to be nonuniformity of packing of the amalgam in the tube due to its very pronounced tendency to stick to the glass. It is felt that this error amounts to about 2%. Homogeneity of the amalgams was checked by measurements before and after further mixing by inverting the sample tube.

The results of the measurements with europium amalgam are presented in Table 2. Columns 1 to 4 list the observed quantities as indicated. The volume susceptibilities in column 5 were calculated from the sample tube calibration factors as described in Part I of this thesis. In calculating the specific susceptibilities (column 6) the density of mercury at the indicated temperature was used. A calculation of the amalgam density assuming additivity of volumes shows that in the worst case the error involved in using the uncorrected density of mercury cannot be greater than 0.5%, which is less than the other errors in the measurements.

TABLE 2

Magnetic Susceptibility of Europium Amalgam

Exp't. No.	(1) Force (mgms.)	(2) Field (oersteds)	(3) Temp. (°C.)	(4) Wt. % Eu	(5) $\kappa_{obs.} \times 10^6$ (c.g.s./ml.)	(6) $\chi_{obs.} \times 10^6$ (c.g.s./gm.)	(7) Europium $\chi_M \times 10^6$ (c.g.s./mole)	(8) μ_{eff}
1	3.9±0.2 / 3.4±0.2	9140 / 8680	25.0±0.1	0.104±0.002	0.47±0.02 / 0.48±0.02	0.035 ± 0.002	29200 ± 1100	8.4±0.2
2	3.3±0.2 / 2.9±0.2	9140 / 8680	25.0±0.1	0.104±0.002	0.40±0.02 / 0.40±0.02	0.030 ± 0.002	28600 ± 1100	8.3±0.2
3	-19.4±0.2	9140	25±1	(6.15 ± 0.3) x 10^{-3}	-2.07±0.02	-0.154 ± 0.002	30400 ± 7500	8.5±1.0
4	50.0±0.2 / 43.9±0.2	9140 / 8680	25.8±0.2	0.307±0.001	5.18±0.02 / 5.25±0.02	0.386 ± 0.002	27300 ± 200	8.09±0.03
5	48.4±0.2 / 42.6±0.2	9140 / 8680	25.1±0.2	0.307±0.001	5.19±0.02 / 5.20±0.02	0.385 ± 0.002	27200 ± 200	8.08±0.03

As the correction for the diamagnetism of the europium is about 30×10^{-6} c.g.s./gm. atom (13) this was neglected in calculating the molar susceptibilities of the europium (column 7). The effective Bohr magneton numbers (μ_{eff}) tabulated in column 8 are recorded only as a convenient method of comparing observed and theoretical susceptibilities (14). The errors indicated are the maximum errors involved in the measurements and do not include the packing error mentioned above.

For comparison Table 3 gives the μ_{eff} value of europium in various states of chemical binding at room temperature, including the aforementioned work of Klemm and Bommer. Included also are the pertinent theoretical values.

TABLE 3

Magnetic Susceptibility of Europium in Various Compounds

Investigator	Chemical State	Oxidation State	μ_{eff}	Theor. or Exper.	Reference
P. W. Selwood	$EuSO_4$ (s)	2	7.66	Exper.	(15)
W. Klemm and W. Döll	$EuCl_2$ (s)	2	7.92	Exper.	(16)
D. L. Douglas and D. M. Yost	$EuCl_2$ (Sol'n)	2	7.94	Exper.	(17)
P. W. Selwood	$Gd_2(SO_4)_3 \cdot 8H_2O$	3	8.11	Exper.	(15)
G. Dupouy	$Eu(NO_3)_3$ (Sol'n)	3	3.20	Exper.	(18)
D. L. Douglas and D. M. Yost	$EuCl_3$ (Sol'n)	3	3.29	Exper.	(17)

TABLE 3

(Continued)

Investigator	Chemical State	Oxidation State	μ_{eff}	Theor. or Exper.	Reference
W. Klemm and H. Bommer	Metal		8.3	Exper.	(2)
J. H. Van Vleck and A. Frank	Eu(III)	3	3.40-3.51	Theor.	(19)
F. Hund	Gd(III)	3	7.9_4	Theor.	(20)

From the close agreement between the effective moments of the Eu(II) and Gd(III) ions one argues that these have the same electronic configuration (outer shells only), namely, $4f^7 5s^2 5p^6$ (21, 22). Klemm and Bommer drew a similar conclusion regarding metallic europium, that is, that the 4f shell is half-filled and the two 6s electrons behave as conduction electrons. The above results with the amalgam of europium support this conclusion. It is, of course, possible that the europium is present in the mercury in the form of an europium-mercury compound. In fact McCoy has reported two such compounds, $EuHg_{10}$ and Eu_3Hg_2 (23). At any rate it is reasonably certain that the europium is present in the plus two state, i.e., with seven electrons in the 4f shell. It would be indeed interesting to study the above mentioned europium-mercury compounds - as regards both magnetic properties and structure.

In Table 4 are given the results of the susceptibility measurements with the amalgams of samarium. All the remarks made relative to the

TABLE 4

Magnetic Susceptibility of Samarium Amalgam

Exp't. No.	(1) Force (mgms.)	(2) Field (oersteds)	(3) Temp. (°C.)	(4) Wt. % Sm	(5) $\kappa_{obs.} \times 10^6$ (c.g.s./ml.)	(6) $\chi_{obs.} \times 10^6$ (c.g.s./gm.)	(7) Samarium $\chi_M \times 10^6$ (c.g.s./mole)	(8) μ_{eff}
1	-15.9±0.2	9140	25.0±0.1	0.323±0.001	-1.55± 0.02	-0.115± 0.002	2360±140	2.38±0.07
2	-14.3±0.2	9140	25.0±0.1	0.375±0.001	-1.51± 0.02	-0.112± 0.002	2160±120	2.28±0.06
3	-14.2±0.2 -12.4±0.2	9140 8680	24±0.5	0.426±0.002	-1.38±0.02 -1.39±0.02	-0.102± 0.002	2250±90	2.32±0.05
4	-11.3±0.2 -10.1±0.2	9140 8680	25±0.5	0.528±0.002	-1.19±0.02 -1.19±0.02	-0.088$_2$± 0.002	2220±90	2.31±0.05

europium case apply here as well, except that the correction for the diamagnetism of the samarium core has been applied to the χ_M values. Because the susceptibility of the samarium is so small, one step in the calculation involves subtraction of two numbers of the same order of magnitude. This, of course, produces a rather larger maximum error in the final result. The excellent agreement among the μ_{eff} values in Table 4 indicates that the probable error is considerably smaller.

To aid in the discussion of these results Table 5 presents a compilation of susceptibility measurements of samarium and its compounds from the literature. The results of a determination of the susceptibility of samarium(III) chloride in HCl solution are given in Table 6 and serve as an index of the purity of the samarium used in this work. In calculating the susceptibility of the samarium(III) ion the diamagnetic susceptibilities listed in Part I of this thesis were used.

TABLE 5

Magnetic Susceptibility of Samarium

at 20° C.

Investigator	Chemical State	Oxidation State	μ_{eff}	Theor. or Exper.	Reference
S. Sugden and S. R. Tailby	$2Sm(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$	3	1.54	Exper.	(24)
P. W. Selwood	$Sm_2(SO_4)_3 \cdot 8H_2O$	3	1.55	Exper.	(25)
P. W. Selwood	$SmBr_2$	2	3.62	Exper.	(25)

TABLE 5

(Continued)

Investigator	Chemical State	Oxidation State	μ_{eff}	Theor. or Exper.	Reference
W. Klemm and H. Bommer	Metal		2.07	Exper.	(2)
A. Frank	Sm(III)	3	1.56	Theor.	(26)
J. H. Van Vleck and A. Frank	Eu(III)	3	3.41-3.51	Theor.	(19)

The close agreement between the susceptibility of samarium(II) and europium(III) indicates strongly that these two ions are isoelectronic, just as in the case of europium(II) and gadolinium(III). The electronic configuration (outer levels only) and term symbol are $4f^6 5s^2 5p^6 {}^7F_0$ (27). Van Vleck and Frank have made the difficult calculation of the theoretical magnetic moment for europium(III) ion, and it is in good agreement with the experimental values. In the case of samarium(III) the configuration and term symbol are $4f^5 5s^2 5p^6 {}^6H_{5/2}$ (27). Here also the calculation of the theoretical moment is quite difficult due to contributions to the magnetic susceptibility from J states other than the lowest. An additional complication arises because some of the levels are split, i.e., some degeneracy is removed by the electric fields of the surrounding ions. However, in 1935 Frank published a paper containing a treatment of the problem which was remarkably successful (26).

While assignment of electronic configuration cannot be made with safety on the basis of magnetic susceptibility measurements alone, it

TABLE 6

Magnetic Susceptibility of Samarium(III) Chloride in Solution

Exp't. No.	(1) Force (mgms.)	(2) Field (oersteds)	(3) Temp. (°C.)	(4) $[(SmCl_3)]$ (moles/liter)	(5) $[(HCl)]$ (moles/liter)	(6) $K_{obs.} \times 10^6$ (c.g.s./ml.)	(7) $\chi_{obs.} \times 10^6$ (c.g.s./gm.)*	Samarium(III) (8) $\chi_M \times 10^6$ (c.g.s./mole)	(9) μ_{eff}
1	-9.1±0.2	9140	27.5±0.3	0.418±0.001	0.241	-0.309			
	-8.1±0.2	8680	27.5±0.3	0.418±0.001	0.241	-0.313			
2	-9.0±0.2	9140	27.5±0.3	0.418±0.001	0.241	-0.311			
	-7.9±0.2	8680	27.5±0.3	0.418±0.001	0.241	-0.310			
Average						-0.311±0.006	-0.283±0.006	1016±10	1.58

* d^{27}_4 = 1.096 gm./ml.

seems clear from the results of Klemm and Bommer and those from the amalgam measurements that in the metallic state samarium is entirely in neither the "plus two" nor the "plus three" configuration. Klemm and Bommer surmise that it is partly in each, a situation which seems unlikely at best. Compound formation in the amalgam cannot be entirely ruled out; but it too seems improbable since the samarium would be present in a mixture of valence states. Perhaps an explanation of this anomaly in the susceptibilities is to be found in a splitting of the lower levels by crystalline fields as in the case of samarium(III). There is not sufficient evidence on hand to test this hypothesis, unfortunately. The experiments which would be necessary are: (1) measurements of the amalgam susceptibility over as wide a range of concentration and temperature as possible and (2) determination of the structures and susceptibilities of samarium-mercury compounds, if any.

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PART III

OBSERVATIONS ON THE CHEMISTRY OF EUROPIUM

A. Preparation of Europium(II) Carbonate

As pointed out by Yost, Russell and Garner europium(II) carbonate plays a particularly important role in the chemistry of bivalent europium (1). Its solubility in most acids makes it a convenient starting point for the preparation of many europium(II) compounds. The only method of preparation of this compound reported in the literature is that of Cooley and Yost (2), in which europium(II) sulfate is boiled with a solution of 1 n. in sodium carbonate and 0.4 n. in sodium hydroxide. The $EuSO_4$ is completely metathesized to the carbonate, which is insoluble in the basic solution. Preparation of the europium(II) sulfate is effected by passing a dilute solution of europium(III) chloride through a Jones reductor (amalgamated zinc) into a sulfuric acid solution (3). The purpose of this investigation was to attempt to shorten this preparation by precipitating the carbonate directly from the solution flowing from the reductor. To this end experiments were carried out in which the reduced europium solution was passed into concentrated solutions of ammonium carbonate.

Experimental

The source and purity of the europium used is discussed in Part I of this thesis. Reagent grade chemicals were used in all experiments. A modified Jones reductor was constructed from a three necked 200 ml. flask.

A glass tube fitted with a stopcock was attached to the bottom of the flask. The contents of the flask were stirred with a nichrome wire "paddle" driven by a low speed motor through the center neck. Glass tubes fitted with a stopper into one of the side necks facilitated the maintaining of a CO_2 atmosphere in the flask. A separatory funnel drained into the flask through a stopper in the other side neck. The outflow tube drained into a conical flask through the stopper of which passed glass tubes. These permitted the flushing out of the air with CO_2. About 100 gms. of c.p. zinc (20 mesh) were amalgamated in the usual manner (4), and placed in the upper flask.

In a typical experiment 15 ml. of 0.05 n. HCl was added to the zinc (enough to cover the zinc entirely) and the mixture stirred for 5 minutes. This was run out the bottom into a beaker and 10 ml. of 0.1 n. europium (III) chloride solution in 0.05 n. HCl was quickly added. After stirring for about 0.5 hr. the reduced europium solution was drained into the conical flask. The latter contained a concentrated ammonium carbonate solution. A precipitate of the light yellow-green europium(II) carbonate formed at once and on heating the mixture it was transformed into an easily filtered product. Immediately the europium solution was drained from the reductor 10 ml. of 0.05 n. HCl was added and the mixture stirred for 5 minutes. This solution was also run into the $(NH_4)_2CO_3$ solution. The precipitate was collected on a 2 ml. sintered glass funnel which had been previously dried and weighed. The filtration was carried out in air. Washing of the precipitate was done as indicated in Table 1. The product was dried in a vacuum desiccator over $CaCl_2$ for a few hours and then in an oven at 110° C. for 1 to 2 hrs.

Analysis of the carbonate for europium(II) was carried out by the

method of H. N. McCoy as described in Part I of this thesis. A weighed amount of the solid was added to a 1.8 n. H_2SO_4 solution containing an excess of $Fe_2(SO_4)_3$ and the iron(II) ion produced titrated with standard $KMnO_4$. In some cases the products were analyzed for total europium by dissolving a weighed sample in hot dil. HNO_3 and precipitating the europium as the oxalate (the hot HNO_3 oxidizes the europium(II) rapidly). The oxalate was ignited to the oxide and the latter weighed.

Results and Discussion

Some typical results are given in Table 1. In order to have a comparison of this procedure with the two step method of Cooley and Yost some $EuSO_4$ was prepared and converted to the carbonate by boiling with a NaOH - $NaHCO_3$ solution as directed. The $EuSO_4$, analyzed by the same method, was 96.5% pure. The carbonate prepared therefrom and filtered and washed in air as above analyzed to be 82.7% $EuCO_3$. It is concluded from this that the filtering and washing operations, when carried out in air, result in some oxidation of the $EuCO_3$ to a normal or basic europium(III) carbonate. The results of the analyses of two of the products for total europium indicated that the oxidized europium was present as $Eu(OH)CO_3 \cdot H_2O$, although the compound $Eu_2(CO_3)_3 \cdot H_2O$ would have been equally satisfactory. The former is considered more likely, but a carbonate analysis would settle the issue. On the basis of the evidence the conclusion is drawn that in order to prepare pure $EuCO_3$ some arrangement is necessary for carrying out the filtering, washing and drying operations in an inert atmosphere.

TABLE 1

Preparation of Europium(II) Carbonate

Number of Experiment	2	4	6	7	8	10	14
Moles Eu(III) x 10^3	1.04	1.04	1.04	1.14	1.09	3.06	3.25
Conc. $EuCl_3$ Sol'n (moles/liter)	0.104	0.104	0.104	0.104	0.104	0.15	0.13
Grams Zinc in Reductor	100	100	100	100	100	100	200
Reduction Time (min.)	30	65	44	45	43	45	45
Conc. of $(NH_4)_2CO_3$ Sol'n (f. wts./liter)	1.5	1.5	2.0	2.0	2.0	2.5	2.5
Volume of $(NH_4)_2CO_3$ Sol'n (ml.)	20	20	30	30	32	40	100
Duration of Digestion at 100° before filtering (min.)					15	15	30
Volumes of Wash Solutions (ml.)							
1 f. $(NH_4)_2CO_3$			10	10	10		
Water	10	10	10	10	10	20	25
CH_3OH	12	12	10	10	10	10	15
Wt. of Product (gms.)	0.224	0.220	0.208	0.236	0.225		
$EuCO_3$ as %	40.4%	59.6%	70.1%	69.0%	79.9%	77.3%	82.0%
Yield of $EuCO_3$ as %	41%	59%	66%	74%	81%		

B. Europium(II) Perchlorate

The stability of dilute aqueous solutions of perchloric acid toward inorganic reducing agents is well known. The complete reduction of perchlorate salts by concentrated solutions of titanium(III) sulfate has been reported, however (5). R. A. Cooley investigated the reaction of 9 n. $HClO_4$ with $EuCO_3$ and found that some reduction does take place (6). Only about 20% of the theoretical amount of chloride ion is formed in the reaction. Cooley also reported the formation of a black, moderately soluble compound; which he presumed to be $Eu(ClO_4)_2$. In an attempt to verify these findings two quantitative experiments were carried out.

In one experiment about 0.3 gm. of 80% $EuCO_3$ was dissolved in 12 ml. of water and just sufficient 60% $HClO_4$ to effect complete solution. The resulting solution was about 0.1 m. in europium(II) perchlorate and displayed the usual yellow-green color. No precipitate of any kind formed. The solution was transferred to a Gouy tube and the susceptibility determined. Some exposure to air occurred during the operation and the solution in the tube was about 0.05 m. in Eu(II) and 0.07 m. in Eu(III). The tube was tightly sealed with a stopper and wax and the susceptibility measured over a period of a week. During this period no appreciable reaction took place.

When a "dry box" became available the following experiment was carried out in an atmosphere of carbon dioxide. Boiled 4.5 m. $HClO_4$ was added dropwise to 0.148 gms. of $EuCl_2$ in a 2 ml. volumetric flask. The only phenomenon observed was the dissolving of the solid $EuCl_2$. After the flask had been filled to the mark and shaken all but a small fraction of the solid went into solution. This residue was probably EuOCl,

formed during the $EuCl_2$ preparation. The solution was allowed to stand about an hour in the CO_2 filled "dry box". A sample was then removed and analyzed for europium(II) as described in Part I of this thesis. The europium(II) concentration found was 0.326 m. This, when compared with 0.332 m., calculated from the amount of $EuCl_2$ and acid used, shows that little if any reduction of the perchloric acid had taken place.

In addition to the above, a few qualitative experiments were performed in which perchloric acid was added to solid $EuCO_3$. Concentrated (60%) $HClO_4$ was found to dissolve $EuCO_3$ very readily, but no Eu(II) could be detected in the resulting solutions. More dilute (10%) $HClO_4$ also dissolved the carbonate and the solutions were found to contain europium(II) ion. Evaporation of the solutions of Eu(II) in 10% $HClO_4$ in a vacuum desiccator resulted in a white solid with no reducing action.

From the experimental results obtained it can be concluded the europium(II) ion is stable in dilute perchloric acid solution for considerable periods of time at room temperature. It also is clear that $Eu(ClO_4)_2$ is fairly soluble in dilute $HClO_4$. Reduction of concentrated perchloric acid by europium(II) ion almost certainly takes place.

C. An Attempted Photochemical Reduction of Carbon Dioxide in Europium(II) Chloride Solutions

The reaction between atomic hydrogen and carbon dioxide in the gas phase has been investigated a number of times (7). Boehm and Bonhoeffer report the formation of formaldehyde as one of the reaction products (8). On the other hand, Taylor and Marshall report no reaction (9). Since atomic hydrogen is an intermediate in the photochemical reduction of water by europium(II) ion, (see Part I of this thesis), the possible reduction of CO_2 to formaldehyde or formic acid in this system was investigated*. The analogy with photosynthesis in plants made this a particularly attractive problem.

Experimental

An apparatus was constructed whereby CO_2 could be bubbled through a tube containing a solution of $EuCl_2$ in 0.5 m. HCl while the system was being irradiated with the light from a mercury arc. Provision was made for removing samples of the solution for analysis. The europium(II) chloride was prepared as described in Part I of this thesis. Tank carbon dioxide was used without further purification. The mercury arc was that described in Part I of this thesis, and the reaction tube was placed within a few cm. of the jacket, no lens or filter system being employed.

Three methods of testing for formaldehyde were considered. Experiments showed that with the Fuschin-Sulfate reagent (10) it was not possible to detect less than 20 micrograms of HCHO. The p-phenylenediamine

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* This problem was suggested by Dr. Oliver Wulf.

spot test (11) was tried and found unsatisfactory as it gave a very high blank with carefully redistilled acetic acid (one of the necessary reagents). Considerably more success was had with the chromotropic acid test (12). This test is specific for formaldehyde and is based on the fact that when this substance is heated with chromotropic acid (1, 8 - dihydroxy naphthalene 3,6 - disulfonic acid) in a 72% sulfuric acid solution a bright violet color appears. The procedure recommended by Feigl is simply to add a drop of the solution being tested to 2 ml. of 72% H_2SO_4, add a little chromotropic acid and after mixing to heat the tube on a water bath at 60° C. for 10 minutes. While the test proved capable of detecting 0.5 microgram of formaldehyde in aqueous solution, the presence of Eu(II) ion was found to prevent the detection of as much as 20 micrograms. This effect occurred in spite of the fact that the europium(II) ion is nearly completely precipitated as $EuSO_4$ from the strong sulfuric acid solution. Europium(III) ion, HCl and NaCl were shown not to be the offenders in separate experiments. The obvious solution to the problem seemed to be to remove the Eu(II) from the solution before carrying out the test. Precipitation of both EuF_2 and EuF_3 by addition of a 0.1 m. NaF solution permitted the detection of less than 1 microgram of HCHO in two drops of the supernatant solution. In all of the above experiments care was taken to exclude oxygen from the solutions. The europium(II) samples were kept in a large beaker from which the air was excluded by a current of CO_2

Two reduction experiments were carried out with 10 ml. of about 0.1 m. $EuCl_2$ in 0.5 m. HCl. The solutions were irradiated for a total of two hours, during which time CO_2 was slowly bubbled through. 0.5 ml. samples were taken for testing before, after and several times during the run.

In some cases two samples were taken and powdered magnesium metal added to one of them. By this technique the test was extended to include formic acid, since this substance is reduced to formaldehyde by magnesium metal in acid solutions. All of the tests were made with two drops of the supernatant solution. The result in every case was negative.

Discussion

The analytical method permitted the detection of 1 microgram of HCHO in about 0.1 ml. of solution. Since only negative results were obtained it is concluded that formaldehyde and formic acid were present at concentrations smaller than 3×10^{-4} m., if at all. Clearly the sensitivity of the test is far from satisfactory.

Any formation of formic acid and formaldehyde must take place through some set of reactions such as the following:

$$H\bullet + H_2CO_3 = HO\text{-}\dot{C}{=}O + HOH \qquad I$$

$$H\bullet + HO\text{-}\dot{C}{=}O = \begin{matrix} HO\text{-}C{=}O \\ | \\ H \end{matrix} \qquad II$$

$$H\bullet + \begin{matrix} HO\text{-}C{=}O \\ | \\ H \end{matrix} = HOH + H\text{-}\dot{C}{=}O \qquad III$$

$$H\bullet + H\text{-}\dot{C}{=}O = H_2C{=}O \qquad IV$$

Given the radicals and molecules above many other reactions are possible, of course. Since these radicals and molecules are present in much smaller concentration than the H atoms the reactions between them will be considerably less probable than the reactions listed. The crucial step in the whole process is reaction I. Using Pauling's 1940 table of bond energies (13), and considering the 42 kcal./mole resonance stabilization energy of

H_2CO_3 (14), the reaction is calculated to be about 2 kcal. endothermic in the gas phase. The heat of vaporization of water being 9.7 kcal./mole, it is probable that the reaction is exothermic in the condensed phase. No estimate of the activation energy can be given, however. Similar calculations show the other reactions to be highly exothermic. Thus if reaction I proceeds to any extent some formic acid, and, to a lesser extent, formaldehyde probably will be formed. Because of the crudeness of the testing method used in these experiments it cannot be concluded that the reaction does not take place at all.

Some improvements in the experimental method can be suggested. In view of the probable formation of hydrogen molecule ion at high acid concentrations, this should be reduced as much as possible. Higher $EuCl_2$ concentrations and a more intense light source should be used.

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PART IV

AGE DETERMINATION FROM CARBON-14 CONTENT: IONIZATION CHAMBER TECHNIQUES

Introduction

The existence of a flux of neutrons in the upper atmosphere has been known for some time (1). There is little doubt that these neutrons are produced by the reactions which take place when cosmic ray primaries encounter the nuclei of the atoms of the atmosphere. In the light of our present knowledge of nuclear phenomena the most probable fate of these neutrons is the loss of their considerable original energy through collisions with air nuclei and finally reaction with these nuclei. The most likely reaction is one with the N^{14} nucleus resulting in the formation of a C^{14} nucleus and a proton. The high probability of this reaction comes, first, from the fact that its cross-section (which contains a probability factor in itself) is far larger than that of most of the other possible reactions, and from the relatively great abundance of N^{14} nuclei in the atmosphere. These observations were first made by S. A. Korff in 1940 (2). Carbon-14 is unstable toward beta emission with a half-life of about 5,600 years.

In 1946 W. F. Libby published a Letter to the Editor in the Physical Review (3) in which he drew some important conclusions from the above. He noted that the C^{14} atoms produced are oxidized by the oxygen of the air and carbon-14 dioxide results. This carbon-14 dioxide is distributed

throughout the atmosphere and is taken up by plants in photosynthesis. In addition it is in equilibrium with the carbonates dissolved in the oceans and lakes and with a part of the earth's rock carbonate. Libby then pointed out that if the cosmic ray intensity has been constant for the last 25,000 to 30,000 years (several times the half-life of the radioactive carbon-14 nucleus) then a radioactive equilibrium will have been established in which the total number of carbon-14 nuclei decaying in unit time is equal to the total number being formed. From the neutron intensity data of Korff and Hammermesh (1) Libby was able to arrive at the estimate of 0.8 neutrons formed per second per $cm.^2$ of the earth's surface. Taking the best estimates he could find of the total amount of plant and animal carbon, atmospheric carbon dioxide, ocean carbonate and rock carbonate Libby estimated that each gram of carbon in exchange equilibrium with the carbon-dioxide in the atmosphere should contain 0.3×10^{-12} gms. of carbon-14. This amounts to about 3 beta particles/min./gm. of carbon.

Libby and his co-workers next concerned themselves with experiments designed to establish the actual amount of carbon-14 in living carbon or "biocarbon" as it is now called (4, 5). It was realized at once that the measurement of such low levels of activity involving a weak beta emitter (155 kev.) would require a special technique. Another approach, not significantly less direct, was to obtain samples of biocarbon and petrocarbon which had been enriched in carbon-13. This enrichment process should result in a great increase in the carbon-14 content of the samples. Samples of pure biomethane were obtained from the Patapsco Sewage Plant of the City of Baltimore. In order to have a control experiment samples of petroleum methane were also procured. Petroleum, being

geologically "old", was expected to show no activity. These samples were enriched in carbon-13 in the methane thermal diffusion plants of the Laboratories of the Houdry Process Corporation at Marcus, Hook, Pennsylvania. A mass spectrometer was used to determine the C^{13} concentration of the samples after enrichment. The C^{14} enrichment was calculated from the operating constants of the column and employing an extension of the separation theory involved. A brass cylinder Geiger counter of about 2 liters capacity and surrounded by 1½" of lead was used to measure the activities. The results obtained are given in Table 1, which is reproduced from the aforementioned papers.

TABLE 1

Activities of Samples Enriched in C^{14} (4, 5)

Source	Sample No.	Calculated C^{14} enrichment	C^{13} Conc. from Mass Spectrometer (%)	% CH_4 in Gas	Date Taken	Total Count rate, includes background (cts./min.)
Petromethane	1	1	1.04	99.6	10/16/46	340.6±1.0
	2	1	1.04	99.6		342.6±1.0
	3	25	6.55	97.2	1/6/47	345.8±1.3
Biomethane	3	1	1.04	99.4	12/5/46	342.9±2.0
	1	10	7.36	93.6	10/17/46	348.7±1.3
	7	32	11.02	99.9	12/2/46	364.0±1.5
	8	260	63.5	97.2	2/10/47	562.0±2.9

These data give a rather elegant proof that Libby's hypothesis is essentially correct. The activity of living carbon is seen to be 10.5 disintegrations/min./gm.

To establish with certainty that the activity is due to C^{14} and not tritium, biomethane sample No. 8 was taken through the chemistry of carbon. The methane was combusted to CO_2, and this was precipitated as $CaCO_3$. Using a screen wall counter the activity was definitely established as being associated with the $CaCO_3$. Further investigation of the beta activity showed its absorption in aluminum to correspond to that of C^{14}. Conversations with the Atomic Energy Commission eliminated the possibility that the C^{14} in Baltimore sewage could have originated in one of the chain reacting piles.

Having proved the existence of cosmic radiation produced carbon-14 in living carbon Libby, Anderson and Arnold next set themselves to developing a method of measuring the activity without having to enrich the samples in a thermal diffusion column (6). The problem was solved to their satisfaction by use of the screen wall counter (7). Preparation of the samples for counting was achieved by carrying out the following steps in the order indicated: reduction to carbon with hydrogen at high temperature, washing of the carbon with hydrochloric acid, combustion of the carbon to carbon dioxide, reduction of the CO_2 to carbon with metallic magnesium and removal of the excess magnesium with acid and water. The carbon samples were spread uniformly over the wall of the counter, giving a layer of 20-25 mg./cm.^{2} in thickness. This thickness is equal to the range of the maximum energy beta particles and is thus "infinitely" thick. A calculation showed that approximately 5.9% of the beta particles

penetrated the carbon with sufficient energy to produce a "count". When shielded with 2" of lead this counter gave a background count of 150 cts./min., far too high to permit reliable measurements to be made on samples of the level of activity involved here. The background was reduced to 10 cts./min. by means of anticoincidence circuits (8) and the provision of 4" of iron shielding inside the lead. This value was lowered to 7.5 cts./min. in later experiments (9). Using this technique, and with the lowest background count, 8 gm. samples were counted with an accuracy of about 5%. The difficulties involved can be emphasized by pointing out that with the most active sample, and with this remarkable lowering of the background, the sample counting rate (= total sample rate less background) was only 75% of the background rate.

By way of application of the technique described above Libby and his co-workers did two things. First, by measuring samples of wood from all over the world they established the fact that the carbon-14 content of living carbon is essentially constant at 12.5 cts./min./gm. throughout the earth (6). When this had been done they made a test of the hypothesis that the age of archeological specimens can be determined by comparing the carbon-14 content thereof with that of recent samples (9). This aspect of the problem should be emphasized somewhat. We have here a beautiful example of the situation in which the techniques of one science can be applied to solutions of the problems of another science. A great many of the specimens collected by archeologists, anthropologists and, to some extent, paleontologists are carbonaceous in nature. Some of these can be "dated" with certainty by standard archeological methods,

but a great majority cannot be placed in time with any reliability whatsoever. Uncertainties of 1,000 years are not uncommon. Since first publishing their work Libby and his co-workers have been literally overwhelmed with samples submitted for dating.

The assumptions on which the application of carbon-14 determinations to age determination rest are three. The first is that the cosmic radiation intensity has been constant within a few percent for the last 20,000 years or so. This applies to long period trends only. Diurnal or seasonal variations in intensity will average out, of course. The second assumption is that samples retain their activity after "death". For cellulose and similar substances this is probably a sound assumption - no exchange of carbon between carbon dioxide and such substances having been suggested or reported in the literature. In the case of solid carbonates (sea shells) the assumption is not valid. It has been conclusively demonstrated that exchange of CO_2 does take place between $BaCO_3$ and gaseous CO_2 (10). At this writing this point is not of great importance since all of the dating samples have been wood or similar materials. The third assumption is that in the enzymatic and other reactions involved in the life processes of plants and animals there is no appreciable isotopic effect on the reaction rates. The general question of the relative reaction velocities of isotopic molecules has just begun to be extensively investigated. Bigeleisen has published a theoretical treatment fairly recently (11). That such an isotopic effect can exist in photosynthesis in plants has been demonstrated by Weigl and Calvin (12). These investigators have shown that at high CO_2 concentrations young barley shoots take up $C^{12}O_2$ more rapidly than $C^{14}O_2$.

However, at the very low concentrations at which CO_2 ordinarily exists in the atmosphere the plant takes up any CO_2 it can find. Much mass spectrographic evidence for the isotopic effect in terrestrial carbon chemistry has been published. An excellent review of this material has been given by K. Rankama (13). It can be concluded from C^{12}/C^{13} ratios determined by the mass spectrograph that little separation of the isotopes exists in the photosynthetic and respiratory reactions by which plants exchange carbon dioxide with the air. There is, however, a definite concentration of the heavier isotope in marine carbonate sediments and of the lighter isotope in carbon compounds in marine organisms. The more subtle questions as to possible isotopic concentrations in particular compounds or classes of compounds in either plants or animals have yet to be investigated. On the basis of this evidence it is probably safe to assume that there exist no isotopic effects of sufficient magnitude to affect the age determination work as long as samples of the same general type, e.g., wood, are used.

To return to the aforementioned work of Libby and Arnold, they measured the activity present in samples of known ages ranging from 2,650 B.C. to 580 A.D. With the exception of the most recent sample (580 A.D.) the agreement between the ages determined from the measured activities and the half-life of carbon-14 and the ages assigned to the samples by the archeologists was excellent. It should be noted that all of the specimens were wood. The principal limiting factor or error in the determination of the age of any sample was the statistical error in the counting rate. The activity levels were so low that a sample had to be counted over a period of about two days to reduce the error in the

reported age to 10%. Encouraged by these results Libby has embarked on an ambitious program of age determination.

When this problem was first suggested to the Institute by Mr. Harold Gladwin it was proposed by Professor H. V. Neher that ionization chambers, such as he had used in cosmic ray studies, might be suitable for this work. Thus the purpose of this research was to investigate the possible use of ionization chambers for the determination of the amount of carbon-14 in living carbon and the extension of these measurements to age determination. To this end a considerable number of experiments were carried out in which ionization chambers were filled with carbon-dioxide from various sources and the rates of discharge of the electroscope system recorded. In order to reduce the background rate the chambers were surrounded by 4" of lead and the instruments and shield installed in the pit beneath Robinson Astrophysics Building. The later measurements were made with the instruments located in one of the lower galleries of Morris Dam. It proved relatively easy to detect the carbon-14 present in living carbon and the method shows promise as regards dating applications.

Experimental

The samples were converted to carbon dioxide by a straightforward combustion in a quartz tube. Figures 1a and 1b show the complete apparatus used. Tank oxygen, passed through $CaCl_2$, soda-lime and concentrated H_2SO_4, was used instead of air to avoid complications due to formation of oxides of nitrogen. The rate of combustion was controlled by mixing tank helium, similarly scrubbed, with the oxygen. Extent of foam

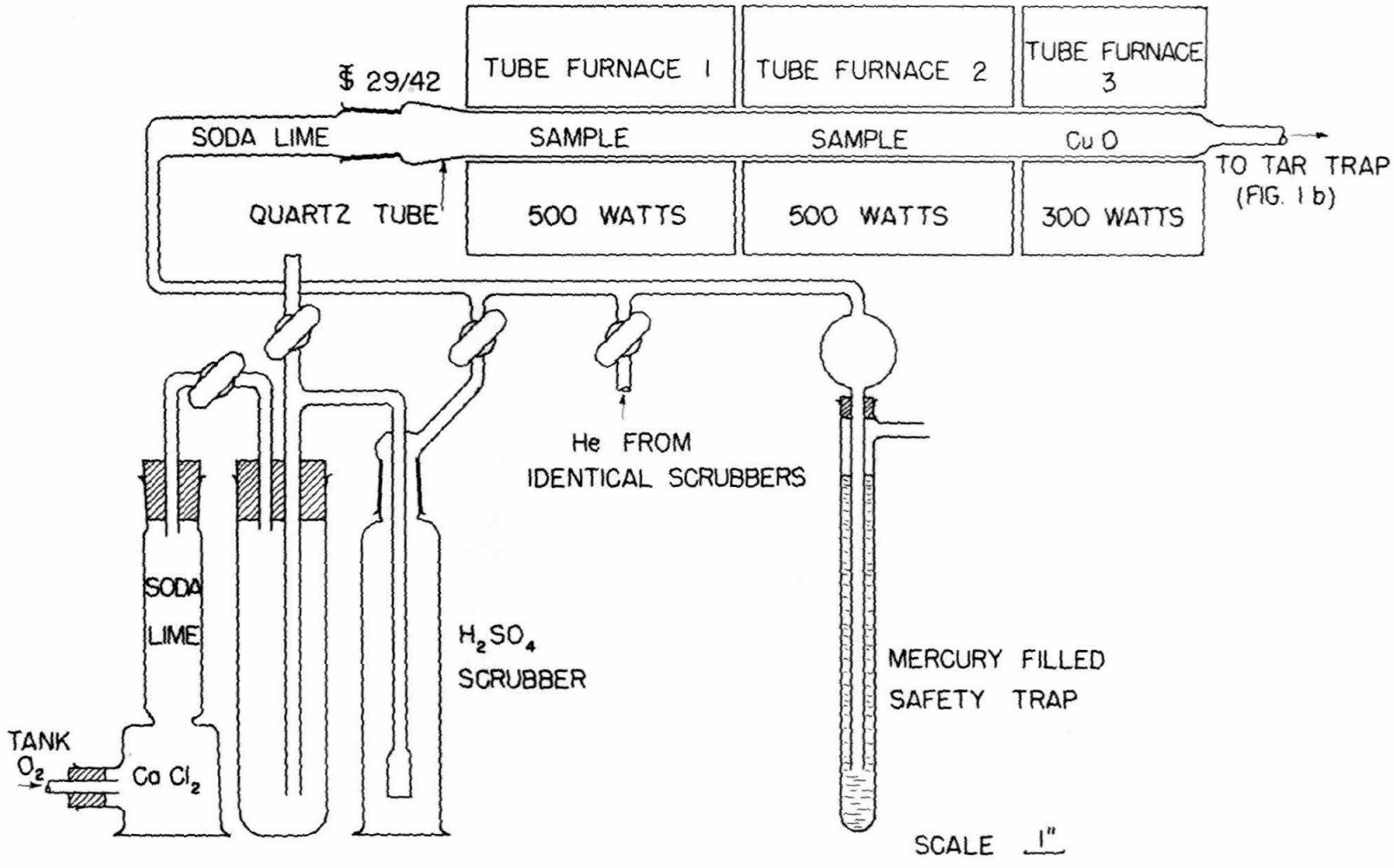

FIGURE 1a. COMBUSTION APPARATUS.

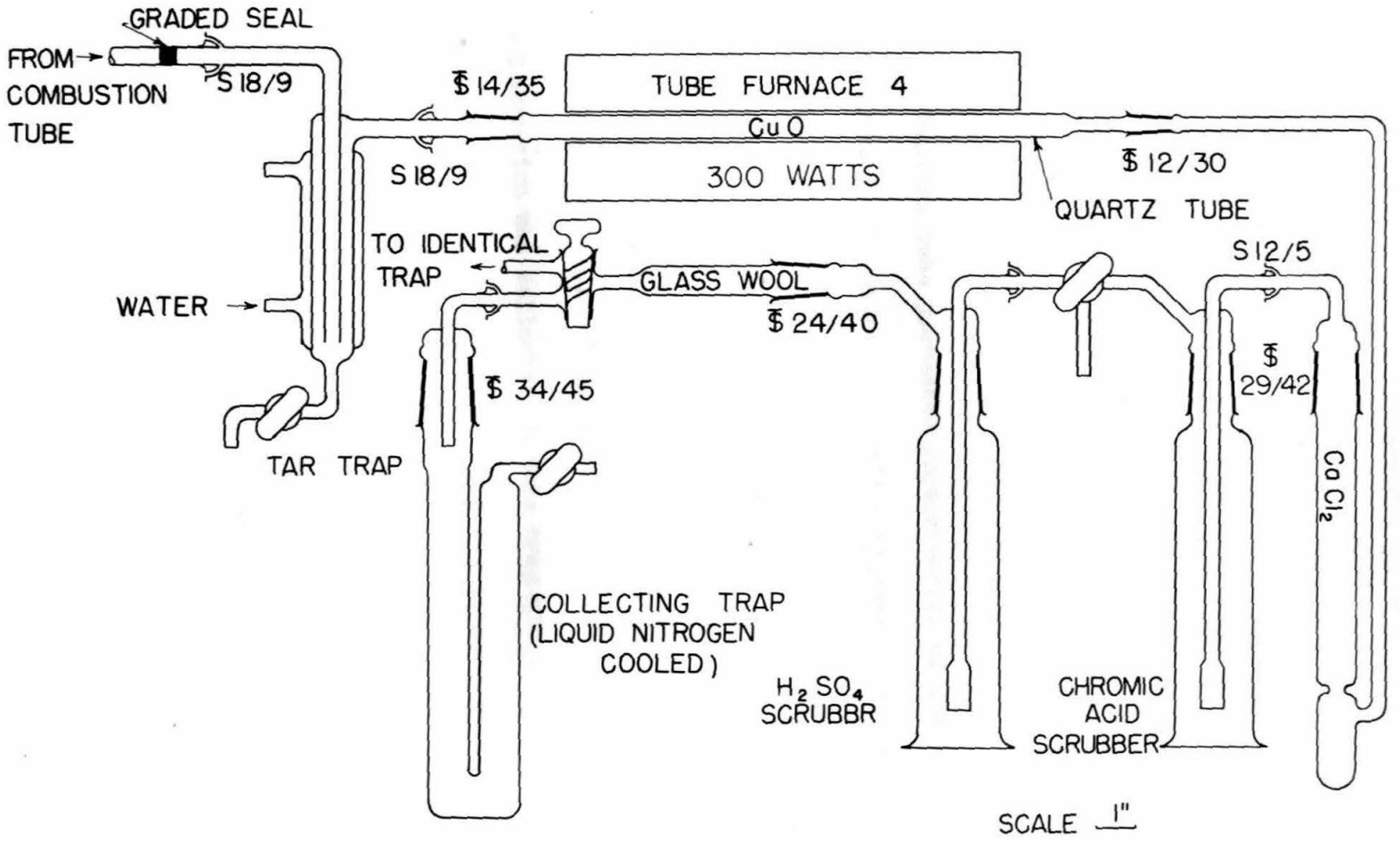

FIGURE 1b COMBUSTION APPARATUS.

formation in the sulfuric acid scrubbers served as a rough index of the relative amounts of the two gases being used. Generally an O_2 to He ratio of one to one was used until the combustion of the sample had started. After that the ratio was increased to 4 or 5 to 1. In this gas mixture, combustion proceeded nicely without overheating the tube.

By cutting the wood samples into small cubes about 1 cm. to an edge 25-30 gms. could be packed into the combustion tube in the section surrounded by furnaces 1 and 2. The soda-lime packed in the pyrex section just before the combustion tube prevented contamination of the scrubbers by combustion products in the event of a sudden pressure rise in the system. Complete combustion to carbon dioxide was aided by the copper oxide fillings surrounded by furnaces 3 and 4, which were maintained at about 600° C. That complete combustion was not attained was evidenced by the accumulation of a small amount of tar in the water cooled tar trap. In no case did the volume of tar exceed 1 cm. Most of the water formed in the combustion was collected in this trap also. Purification of the carbon dioxide was achieved by passing it over calcium chloride and then through a chromic acid (H_2SO_4 + $K_2Cr_2O_7$) scrubber and finally through a sulfuric acid scrubber. In the course of a combustion the chromic acid was changed from a dark red-brown solution to a greenish-black. Undoubtedly some reducing substances managed to get through. Since the sulfuric acid in the last scrubber always remained perfectly clear it is probable that the first scrubber absorbed these substances completely. One or two combustions were carried out with the omission of $K_2Cr_2O_7$. The first scrubbing solution became dark but the second remained clear. However, in these cases, some NO was observed (blue color) in the final product - which situation never occurred when

chromic acid was employed. Since nitrogen is a constituent of all natural materials the presence of NO was not surprising. Its removal by the chromic acid probably proceeded by two paths, first, by oxidation to the soluble NO_2 by the chromic acid, and, second, by formation of stable complexes with the chromic ion resulting from the reduction (14). After passing through a glass wool plug to remove any sulfuric acid mist the CO_2 was collected in U-tube traps cooled with liquid nitrogen.

After sufficient CO_2 had been collected in one of the traps the latter was transferred to the vacuum system, Figure 2, for further purification and collection of the gas. The first step in this process consisted in again immersing the trap in a liquid nitrogen filled Dewar flask and pumping out the air. In all cases a Welch "Duo-Seal" 2-stage pump was used for evacuation. When protected by a cold trap this pump is reputed to produce a vacuum of better than one micron - more than sufficient for these purposes. After pumping the air out of the trap, and the rest of the system, of course, the carbon dioxide was distilled through the system and frozen in the final collecting trap with liquid nitrogen. The dry-ice acetone cooled trap removed the less volatile impurities, e.g., H_2O, H_2S, NO_2 and SO_2. Complete drying was insured by the P_2O_5 towers. The rate of evaporation of the CO_2 was regulated so that the pressure in the system remained at about 1 to 2 mm. of mercury. This was somewhat time consuming, but the efficiency of the trap and drying agents is greater at lower pressures. After the distillation was complete the CO_2 was transferred to a storage cylinder connected at the point indicated in Figure 2. These "bombs" are simply U.S. Air Force

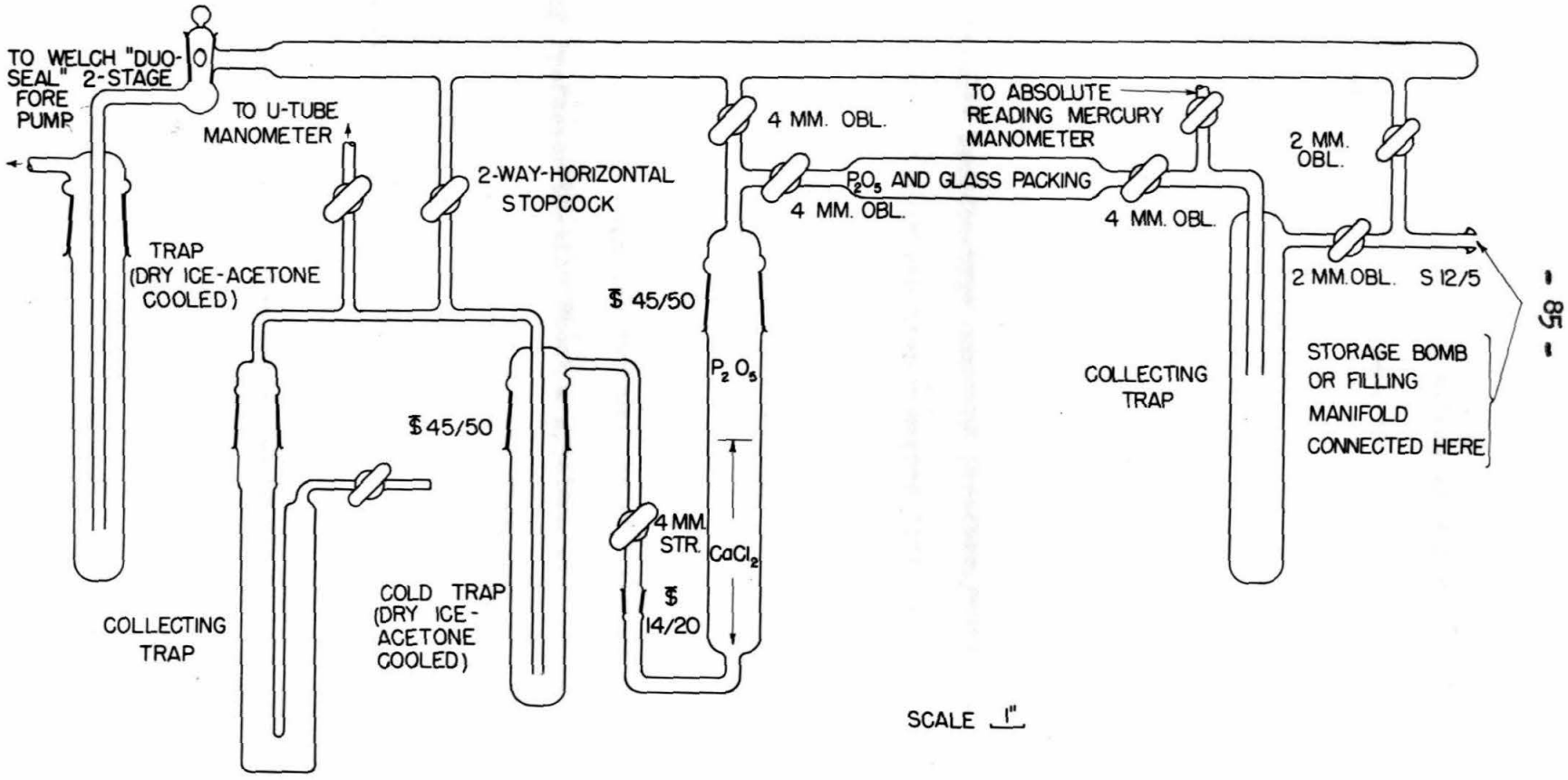

FIGURE 2. VACUUM SYSTEM.

"bail out" oxygen cylinders* and have a volume of 332 cm.^{3}. The only adaptations found necessary to make them suitable for use here were to replace the filling plug with a copper tubing fitting and to seal the outlet through the stem. The valves, of the ordinary packing type, proved capable of holding both vacuum and pressure without significant leakage.

The filling of the chambers was done through a simple manifold arrangement. One arm of a 1/8" pipe "tee" was connected to the vacuum system through a high pressure valve. The other arms led to the CO_2 bomb, a Marshalltown** bourdon-type compound pressure gauge and the chamber, respectively. All of the high pressure lines were made from 3/16" copper tubing - standard "flare" fittings being employed. The manufacturers of the gauge claimed an accuracy of 1/2 of 1% in the range about 150 psi. The maximum scale reading of the gauge was 300 psi and care was taken never to use it above 225 psi.

Other than combustible samples two sources of CO_2 were used. Through the kindness of Professor Chester Stock a specimen of limestone was obtained. This was converted to CO_2 in a small Kipp generator. Before collection in the U-tube traps the gas was scrubbed with conc. H_2SO_4. Subsequent treatment of the product was just as described for the combusted samples. Since the combustions required a considerable amount of time and attention consideration was given to tank CO_2 as a more convenient source. A conversation with a representative of the Pure Carbonic Corp., Los Angeles, California, revealed that all tank carbon dioxide in this area is produced from "stack gas", i.e., as a by-product

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* The kindness of Professor H. J. Lucas in supplying these cylinders is gratefully acknowledged.

** Marshalltown Gauge Co., Marshalltown, Iowa.

of the combustion of coke and oil. A considerable use was made of this geologically "old" carbon dioxide in the earlier experiments. Prior to use it was purified in exactly the same way as the other samples.

As was previously mentioned the ionization chambers are of the type used in cosmic ray studies. A partial description of the instruments is given by Millikan and Neher (15). Photographs of the device are presented in Figures 4a and 4b. The spherical end (vol. = 1776 cm.3) is the chamber proper. This is connected to the camera by the optical tube. Glass windows permit a beam of light to traverse the chamber and travel down the tube to the camera. In the center of the spherical cavity is located the quartz electroscope system, a diagram of which is given in Figure 3 (16). On charging the system to about 300 volts the electrostatic forces repel the vane from the stationary arms in the manner indicated. As the ions are collected and the charge decreased the torsion fiber returns the vane to its original position. A system of lenses located within the chamber brings the image of the hook on the end of the vane* to a focus on a horizontal slit at the camera end of the optical tube. This image is, of course, a shadow. As the motor moves the film (standard 35 mm. motion picture film) past the slit all of the film is exposed except the point covered by this shadow. If the position of the vane is changing, as it is when the charge on the electroscope is changing, the sum of the two motions is a slanting trace or line on the film. At a constant film speed the slope of the trace is a measure of the rate of discharge of the electroscope. The clockwork motors originally provided with the instruments were replaced by Hayden synchronous timing motors. While the shaft from the motor gear box revolved at

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* Improperly labelled "fiducial point" in Figure 3.

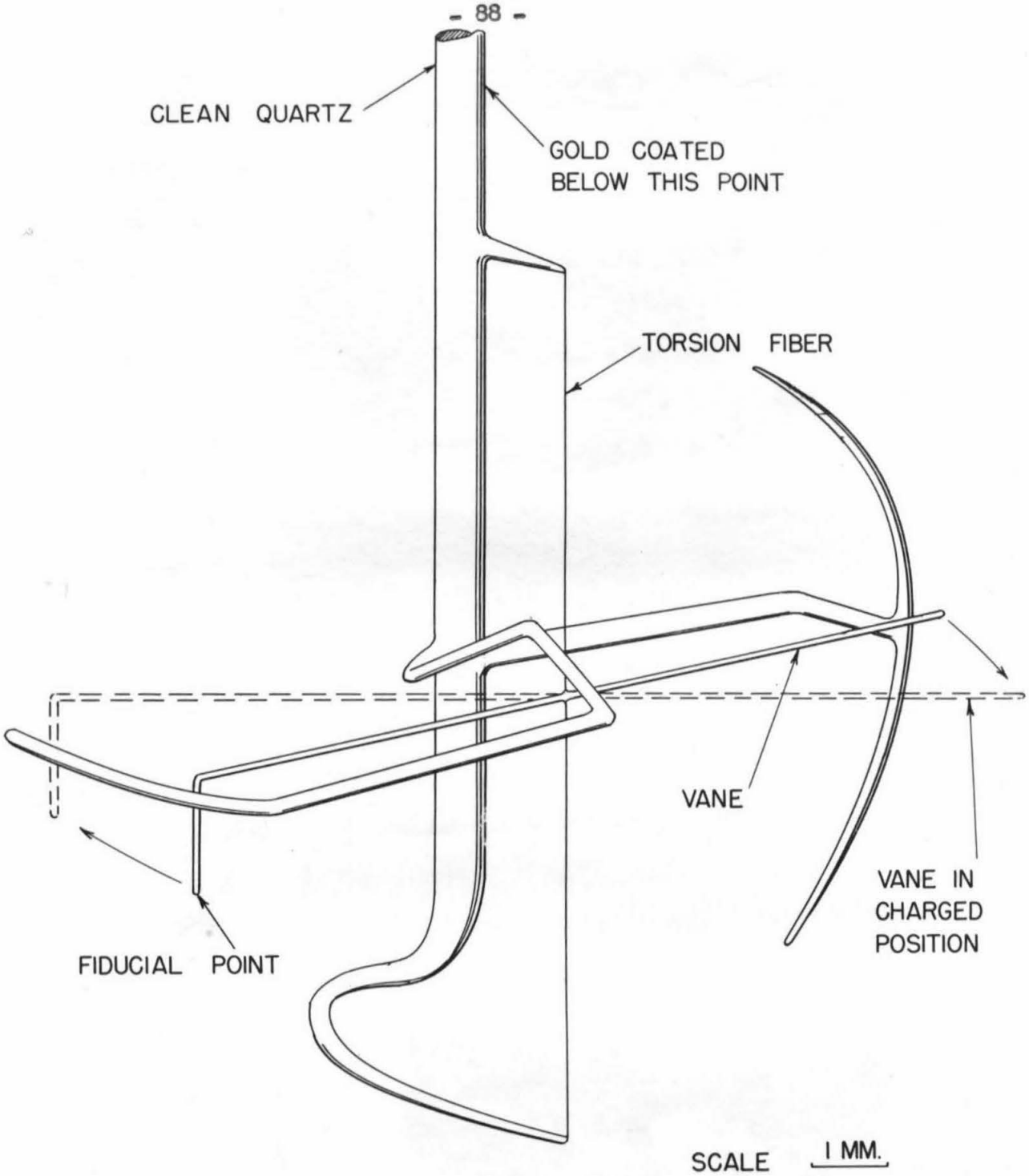

FIGURE 3. ELECTROSCOPE

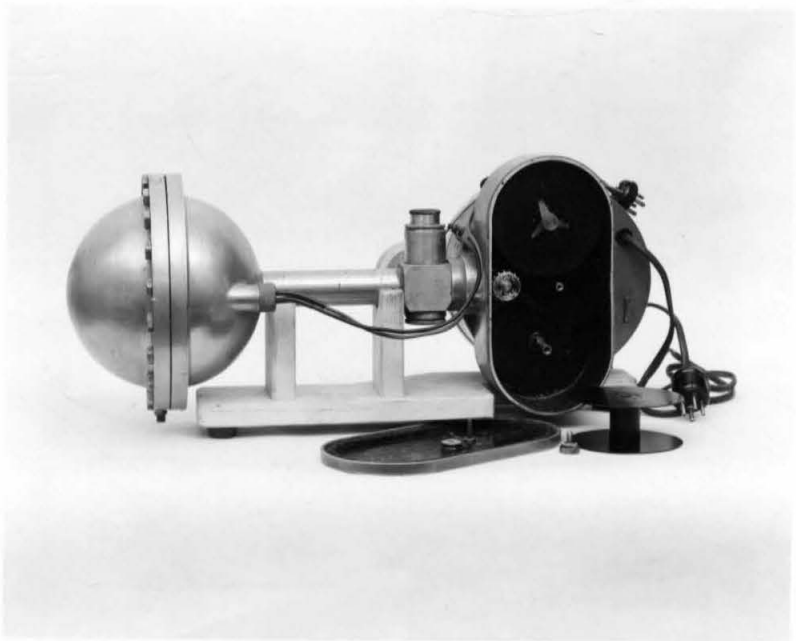

Figure 4a Ionization Chamber

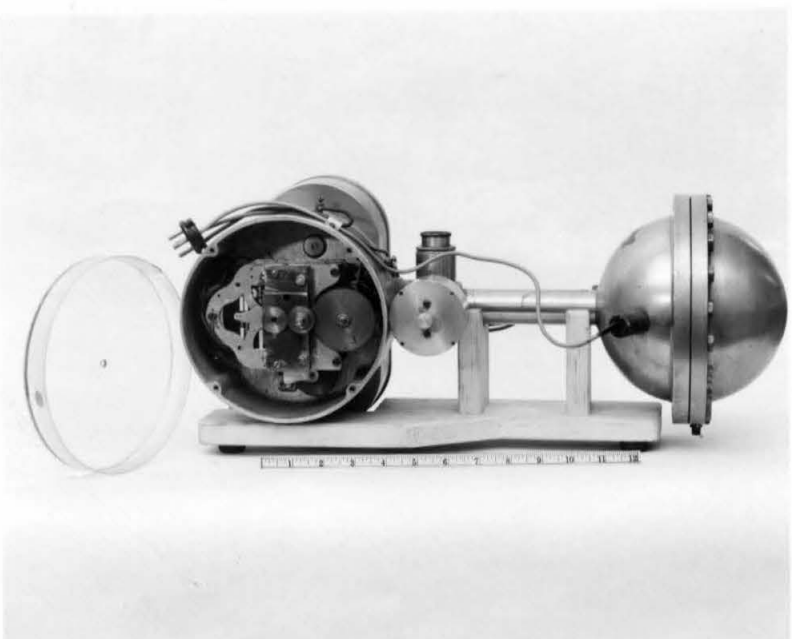

Figure 4b Ionization Chamber

2 rev./day a set of interchangeable gears permitted the speed of the film to be varied over a considerable range.

Besides the glass windows only the high voltage lead (Figure 4b) and the filling port penetrate the chamber walls. The former is well insulated, of course. The latter is set in one of the flanges, and the combination plug and valve can be seen at the bottom of the sphere in both Figures 4a and 4b. An arm with a fine wire extension carries the high potential to the electroscope, contact being made at a platinum collar at the end of the gold coating. The charging arm, normally held away from the electroscope by a spring, is activated by an external solenoid. A re-entrant cylindrical cavity holds the coil of the solenoid, and the iron core moves in a smaller cavity re-entrant from the inside of the chamber. The leads to the coil can be seen in Figure 4a. Periodic recharging of the electroscope is attained through a 4-contact rotary switch revolving with the film sprocket. Thus the voltage interval, through which the electroscope is permitted to discharge, is set when the film speed is chosen. The high potential used to charge the electroscope is supplied by a 300 volt "B" battery* and the power for the solenoid by three or four 1½ volt dry cells in series. These batteries are set in a wooden box which contains, in addition, a sensitive relay. The coil of this relay is in series with that activating the charging arm. When the rotary switch makes contact the two solenoids are activated. The relay in the box completes the 300 volt circuit to the electroscope. When the rotary switch is open this relay keeps the charging arm at ground potential.

The films were developed and fixed in the usual manner. After

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* Everready Minimax No. 493 or Burgess U-200.

drying the slopes of the traces were read off and recorded. In nearly all cases the slopes were determined by placing the films, sandwiched between plates of glass, in the library microfilm reader. A piece of graph paper glued to a piece of Masonite placed in the bottom of the "reader" provided a very convenient way of measuring the slopes. In some cases, either due to poor focusing or to overexposure of the films, it was necessary to resort to a "travelling" microscope to measure the slopes. To check the optics of the microfilm reader some of the slopes determined with it were remeasured with the travelling microscope. The values obtained with the two methods were the same within the experimental error. Since the slope reading could suffer from some subjective error the slopes from one or two films were checked by another observer. No significant differences were found.

A general discussion of the background problem will be given later, but at this point it is appropriate to describe the two instrument locations used. The cosmic radiation contribution to the background ionization observed in the chamber can be reduced only by covering the instrument with a sufficient amount of material, e.g., earth, water or concrete, to absorb an appreciable fraction of the meson secondaries. The locations used in these experiments were selected with this in mind. The first experiments were carried out with the instruments and lead shielding placed at the bottom of the vertical shaft under the Robinson Astrophysics Building. Hereafter this location will be referred to as the "astropit". In essence the pit consists of a rectangular well 8'0" x 24'4" in cross section and 54'0" deep - measured from the floor of the second sub-basement of the building. The opening subtends a

solid angle of 6.69×10^{-2} stearadians at the floor. Since the shielding offered by this location was considered insufficient a second, the 937' gallery in Morris Dam, was used in the later experiments. Figure 5 is a plan view of the dam and shows the location of the instrument relative to the portal and to the upstream face of the dam. Figure 6 presents a section through the dam at the position of the instrument. Taking the specific gravity of concrete as 2.5 one sees from Figure 6 that at least 100 meters equivalent of water lies above the instrument location in all directions.

In order to obtain from the slopes of the traces the rates of discharge of the electroscopes in terms of volts per unit time it was necessary to calibrate the instruments. Unfortunately this could be done only in the following relatively crude manner. The potential applied to the electroscope was varied stepwise over the 40 to 50 v. range which allowed the image of the vane to completely traverse the film. At each voltage the position of the image on the film was established by putting a bright light close to the chamber window and turning the film drive by hand. Placing the film in the microfilm reader permitted conversion of the change of vane position with voltage to the arbitrary units of the reading chart. A plot of voltage against position of the image in these units showed a relationship that was very closely linear. This was the expected result inasmuch as the electroscopes were designed to show this characteristic. The slope of this line was one of the two factors needed for the desired conversion. The second factor was obtained from the distance on the reading chart parallel to the motion of the film corresponding to the time interval between chargings of the

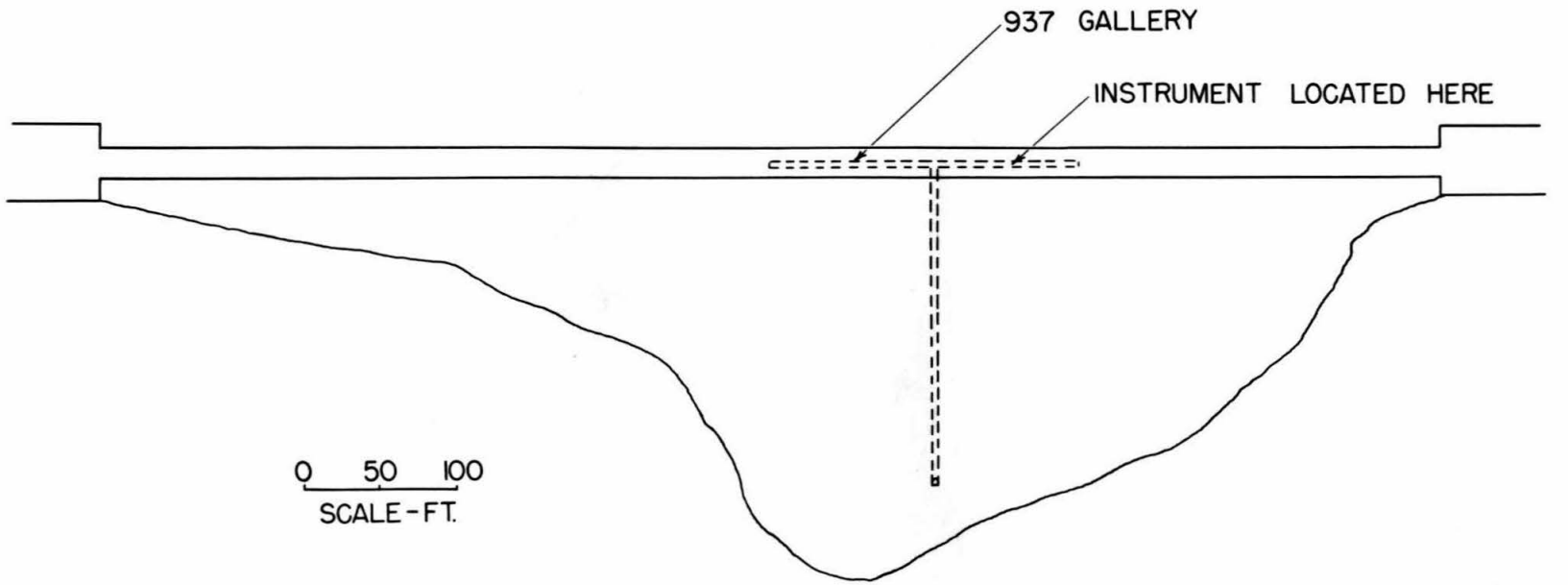

FIGURE 5. MORRIS DAM LOCATION - PLAN VIEW.

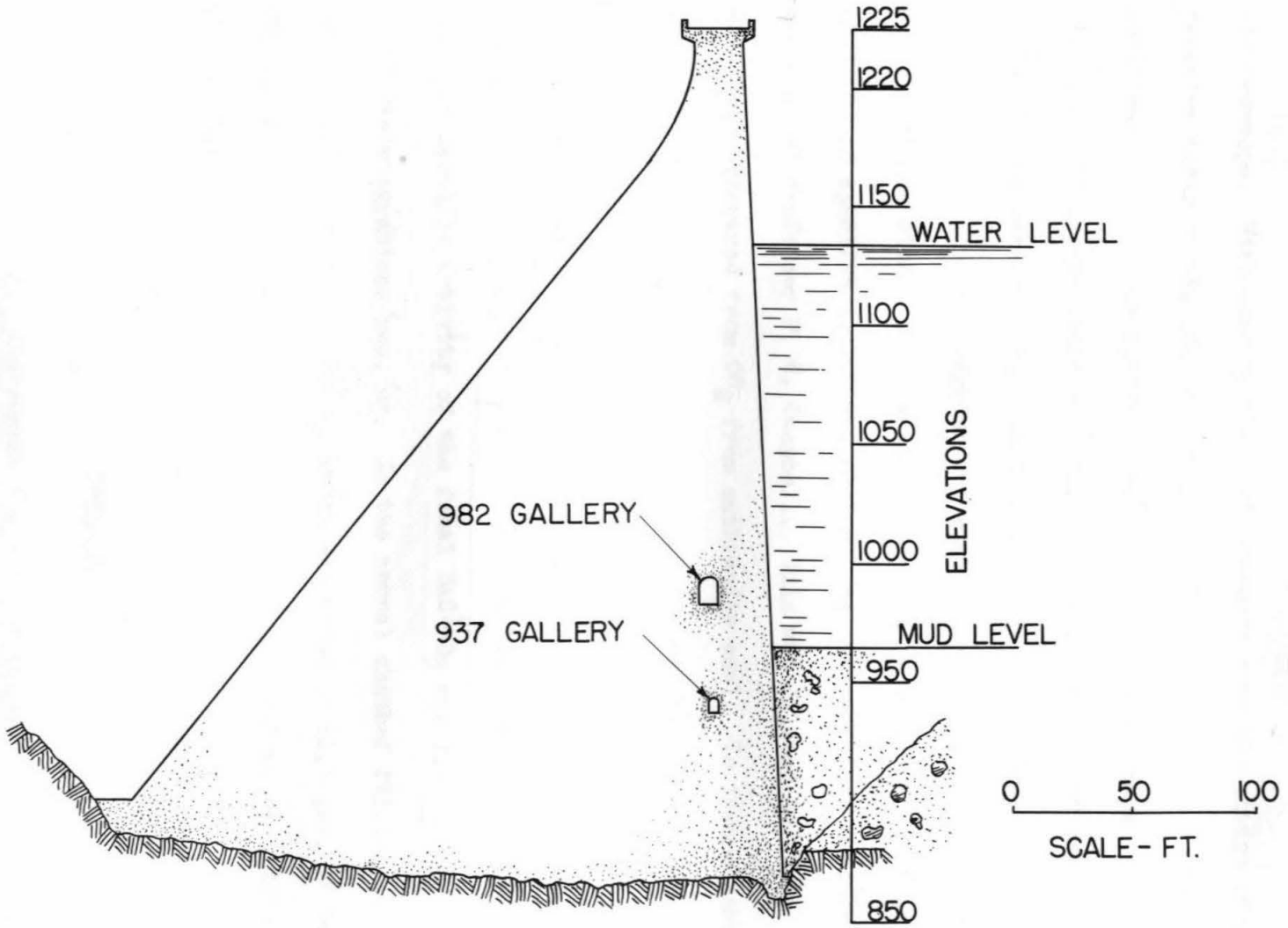

FIGURE 6. MORRIS DAM LOCATION - CROSS-SECTION.

electroscope. With some of the high pressure runs the change of refractive index of the CO_2 was sufficient to require the placing of an additional lens in the optical tube to keep the vane image focused on the film. Since the voltage calibration is a function of the optical system it was necessary to recalibrate for each lens arrangement.

One experiment was carried out with geologically "old" carbon dioxide enriched with a known amount of $C^{14}O_2$. A small amount (1.15 mg.) of $BaCO_3$ of specific activity 0.0115 mc./mg. was obtained through the kindness of Professor D. H. Campbell. This was diluted by mixing it with $BaCO_3$ prepared from CO_2 from anthracite coal. To insure complete mixing the carbonates were converted to CO_2 and the gas trapped in sodium hydroxide solution. The carbonate ion formed was reconverted to $BaCO_3$ in the usual manner. Two dilutions were carried out, reducing the specific activity of the carbonate by a total factor of 1.0×10^{-4}. Thus the specific activity of the final $BaC^{14}O_3$ was 1.15×10^{-6} mc./mg. or 42 disintegrations/sec./mg. In the actual chamber filling 1.11 mg. of this was converted to $C^{14}O_2$, which was added to 41.1 gms. of tank CO_2 in one of the bombs. Only 32.5 gms. of the mixture was added to the chamber.

Results

A. Instrument No. 1 in "Astropit"

Only one instrument was available for the first experiments, and this is referred to as No. 1. Another was assembled later on and is designated No. 2. A graphical summary of the results obtained with No. 1 in the "astropit" is given in Figure 7. The pertinent data from

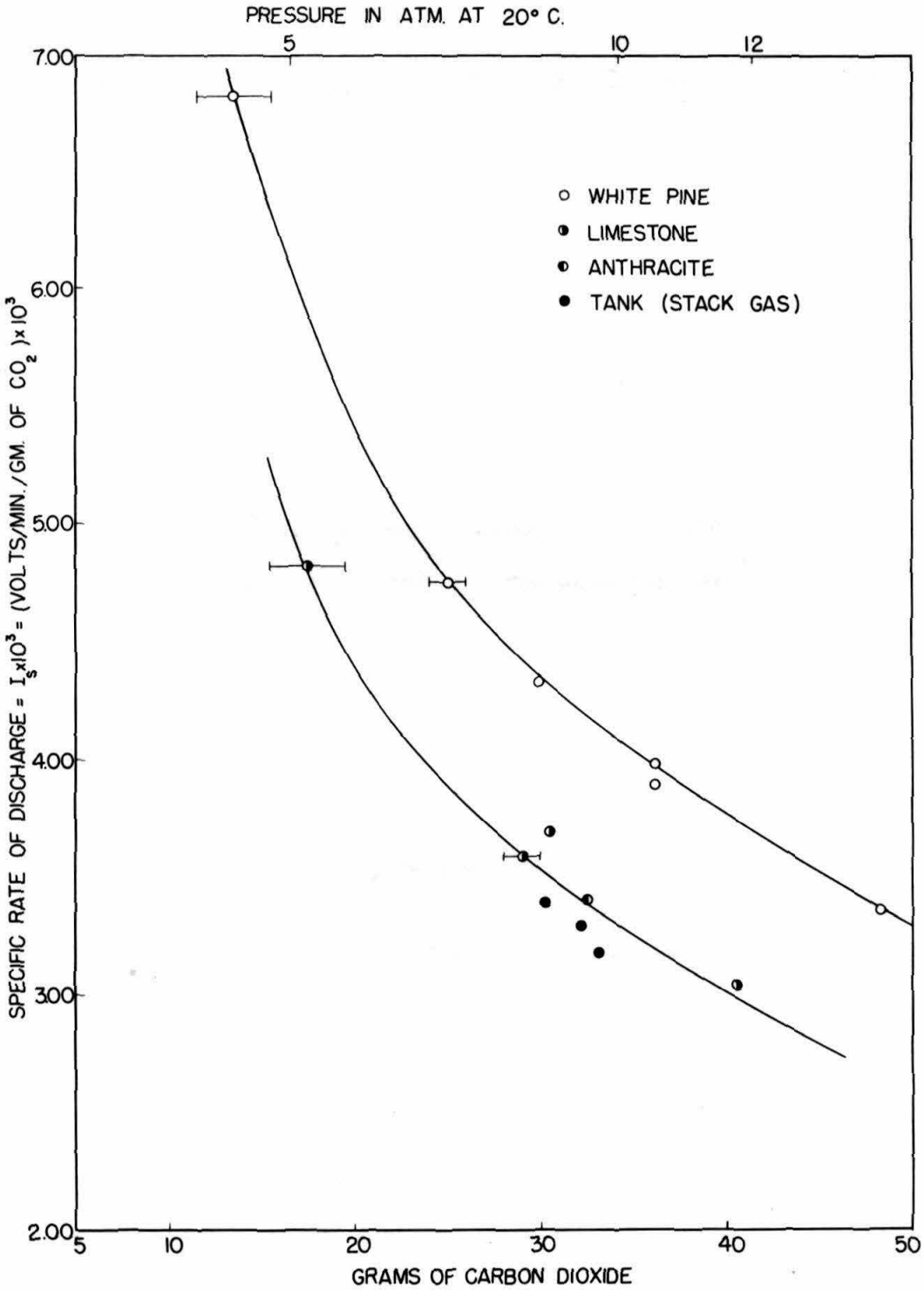

FIGURE 7.
SPECIFIC RATE OF DISCHARGE OF ELECTROSCOPE
VS. GRAMS OF CARBON DIOXIDE
INSTRUMENT NO. 1 IN ASTROPIT

these experiments are summarized in Table 2. In this table column (1) gives the experiment number and film number in that order. Column (2) lists the number of traces obtained and used in the calculations. Column (3) describes the chamber filling. Columns (4) and (5) indicate the amount of gas in the chamber in grams and atmospheres pressure, respectively. In most of these experiments the amount of gas admitted to the chamber was determined by weighing the bomb before and after filling. The weights listed are probably reliable to 0.1 gm. The pressures were calculated by use of van der Waals' equation ($a = 5.007 \times 10^6$ cc.^{2} atm./mole, $b = 104.8$ cc./mole) for 20° C. The time interval, after which the electroscope was recharged, is given in column (6). The average slope of the traces is tabulated in column (7). The average deviation of the mean in only two cases was greater than 0.002, and for all but four films was equal to 0.001 or less. I_v (column 8) was calculated from the slope and the two calibration factors thus:

$$I_v = \text{slope} \times \frac{22.4 \text{ chart divisions}}{\text{time base}} \times \frac{3.85 \text{ volts}}{1 \text{ chart division}}.*$$

Column (9) gives the specific rates of discharge, I_s, calculated by dividing column (8) by column (4). These values should be a measure of the amount of activity, i.e., C^{14}, present in the carbon dioxide. Concerning the samples used: the "white pine" was merely a scrap of lumber

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* The voltage calibration factor, 3.85, is doubtless very much in error. The chamber was taken apart twice and the positions of one of the lenses and of the electroscope altered slightly, after these experiments were carried out and before the voltage calibration was done. This should not affect the relative reliability of the results, however.

TABLE 2

Instrument No. 1 in "Astropit": Summary of Data and Calculations

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Time Base (min.)	(7) Average Slope	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
---6	4	Argon		10	180	0.452		
---7	7	Argon		10	180	0.454		
---8	15	Argon		10	180	0.470		
---9	15	Argon		10	180	0.473		
2-11	8	White Pine	48.2	13.9	180	0.337	16.1_5	3.35
2-12	4	White Pine	48.2	13.9	180	0.339	16.2_5	3.37
2-15	4	White Pine	25 ± 0.8	7.4	180	0.248	11.9_0	4.76
2-16	7	White Pine	25 ± 0.8	7.4	180	0.247	11.8_4	4.75
2-17	7	White Pine	13.5 ± 1.6	4.1	180	0.192	9.2_0	6.82
3-18	13	Anthracite	32.5	9.5	180	0.232	11.1_1	3.42

TABLE 2

(Continued)

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Time Base (min.)	(7) Average Slope	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
3-19	10	Anthracite	32.5	9.5	180	0.229	10.9_8	3.38
4-20	24	Limestone	30.4	8.9	180	0.234	11.2_1	3.69
5-21	6	Limestone	40.5	11.7_5	180	0.257	12.3_2	3.04
5-22	8	Limestone	29 ± 0.8	9.8_5	180	0.217	10.4_0	3.59
5-23	6	Limestone	17.5 ± 1.6	5.3	180	0.176	8.4_4	4.82
6-24	7	Tank	33.1	9.7	180	0.218	10.4_5	3.16
6-25	7	Tank	33.1	9.7	180	0.219	10.5_0	3.17_5
6-26	7	Tank	33.1	9.7	180	0.220	10.5_5	3.19

TABLE 2

(Continued)

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Time Base (min.)	(7) Average Slope	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
7-27	9	$C^{14}O_2$	32.5	9.5_0	100	0.630	54.3	16.70
7-28	13	(37 cts./sec.)	32.5	9.5_0	100	0.632	54.5	16.76
8-29	10	Tank	32.2	9.4_2	180	0.221	10.6_0	3.29
9a-32	11	White Pine	36.1	10.5_4	180	0.293	14.0_5	3.89
9b-33	13	White Pine	29.9	8.7_6	180	0.270	12.9_5	4.33
10a-34	5	Tank	30.2	8.8_5	600	0.713	10.2_5	3.39

from the wood shop; "anthracite" refers to a poor grade of anthracite coal collected from a local coal yard; the limestone and tank CO_2 have been previously discussed.

It is clear from Figure 7 and Table 2 that the CO_2 from the white pine contains a significant amount of radioactivity. That this is the same phenomenon observed by Libby and his associates can be shown by the following calculation. At 30 gms. of CO_2 the discharge caused by the C^{14} is 0.81×10^{-3} v./min./gm. of $CO_2 = 2.96 \times 10^{-3}$ v./min./gm. of carbon. The capacitance of the electroscope system is about 0.5 cm. or 0.56×10^{-12} farads (17). From these values one calculates that 1.66×10^{-15} coul. of charge are collected per minute. This is equal to 1.04×10^{4} singly charged ions, i.e., electrons, and hence this many ion pairs must be formed in the chamber every minute. Taking the mean energy of the electrons emitted by the decaying C^{14} nuclei as 50 kev. (18) and the average energy lost per ion pair formed in the CO_2 as 30 e.v., one obtains 6.2 disintegrations/min./gm. of carbon as the specific activity of the CO_2 from the white pine. This is slightly smaller than the activity reported by Libby, but considering the approximations involved the agreement is very satisfactory. One possible explanation for the low value is that volume recombination of the ions is taking place to a considerable extent. This hypothesis receives some support from the fact that the number of ions collected in the "astropit" decreased by a factor of two on changing the filling from argon to carbon dioxide (Table 2). However, the fact that the curves for biocarbon dioxide and petrocarbon dioxide parallel one another up to 20 atmospheres argues against this explanation, since volume recombination should increase with pressure.

The data from the experiment with $C^{14}O_2$ permit another determination of the activity in the white pine CO_2 to be made. From Table 2, page 100, we see that the activity in the chamber amounts to 37 cts./sec. This is equivalent to 250 disintegrations/min./gm. of carbon in the chamber and produces a discharge rate of 43.4×10^{-2} v./min. above background. If it is assumed that the recombination effect is the same at the two levels of ionization, then the white pine CO_2 (2.56×10^{-2} v./min. above background at 32.5 gms. of CO_2 in the chamber) has a specific activity of 14.8 cts./min./gm. of carbon. This figure is in somewhat better agreement with Libby's value of 12.5 cts./min./gm. It should be noted that some loss of activity occurred in the dilution experiments, so the figure 14.8 cts./min./gm. is undoubtedly high. All in all it is clear that the results effectively confirm those of Professor Libby.

B. Experiments in Morris Dam

It was evident that the ratio of sample activity to background is so small in the "astropit" that impracticably long "counting" times would be required to reduce the statistical error to an acceptable value. The discharge rate in the "astropit" with the argon filling, when compared with the rate at the surface*, showed that the total background ionization was reduced by a factor of one-fourth. In an attempt to further cut down the cosmic radiation contribution to the background experiments were carried out in Morris Dam. As indicated on page 92 of this thesis the shielding afforded by this structure and the water behind it is equivalent to at least 100 meters of water. This should reduce the ionization caused by cosmic ray mesons to approximately 2% of its sea level value (19). A complete discussion of the background question will be presented below.

The first experiments carried out in Morris Dam had the purpose simply of comparing the location with the "astropit". The data obtained have provided very important information concerning the various contributions to the background effect. White pine and tank CO_2 were once again the chamber fillings employed. Figure 8 presents the results in graphical form, and Table 3 summarizes the data and calculations involved. The remarks made concerning Table 2 apply to Table 3 as well. In all cases the average deviation of the slope was 0.002 or less. The amount of gas in the chamber was determined by the weighing method in experiments 10b through 12. The pressure gauge previously described was used

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* Information as to the rate of discharge of the electroscope at the surface was supplied by Professor H. V. Neher.

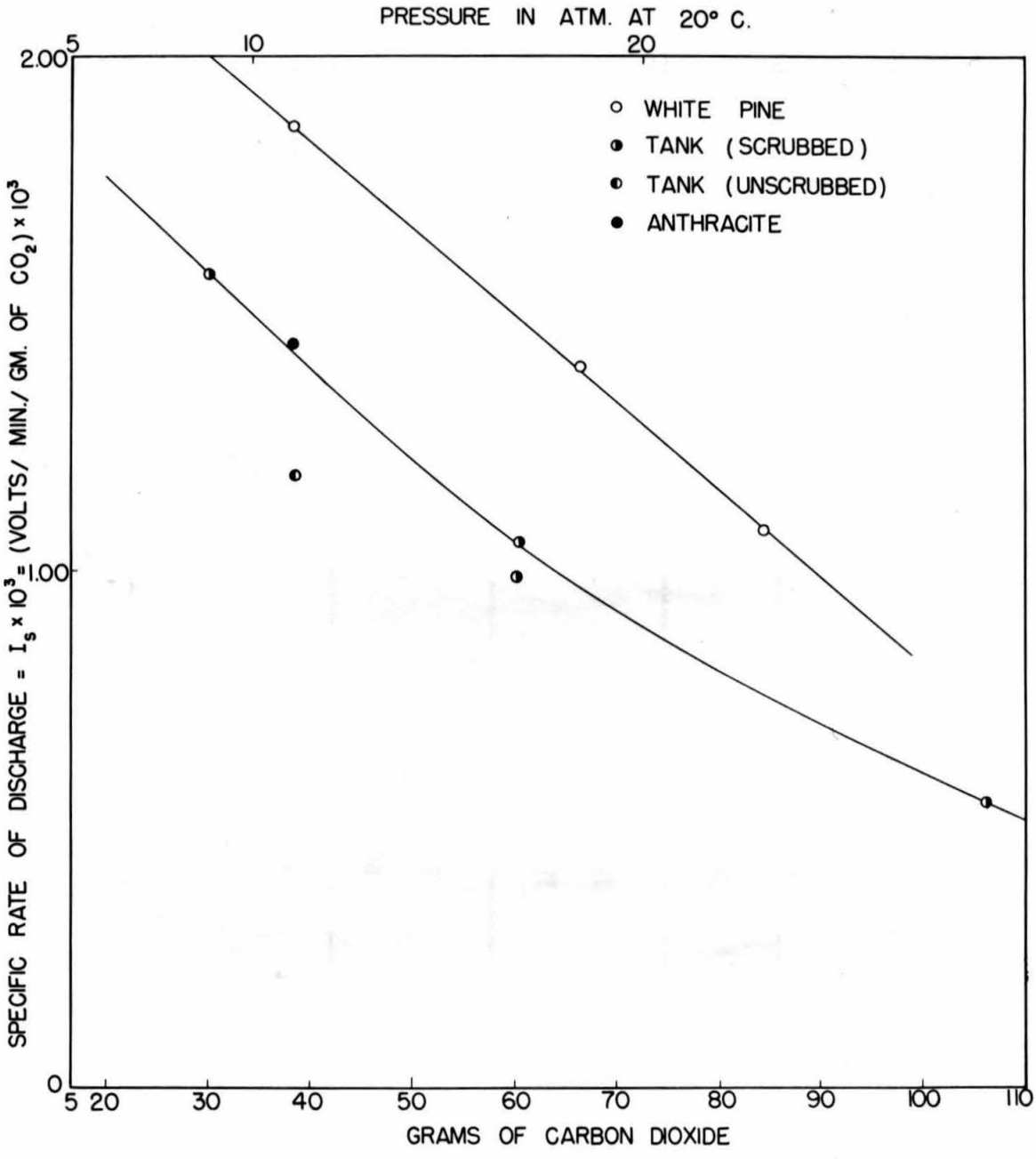

FIGURE 8.
SPECIFIC RATE OF DISCHARGE OF ELECTROSCOPE
VS. GRAMS OF CARBON DIOXIDE
INSTRUMENT NO. 2 IN MORRIS DAM

TABLE 3

Instrument No. 1 in Morris Dam: Summary of Data and Calculations

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Time Base (min.)	(7) Average Slope	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
10b-35	3	Tank	30.2	8.85	600	0.330	4.74	1.57_0
10b-36	8	Tank	30.2	8.85	600	0.333	4.78	1.58_3
11-38	7	Tank	50.3	14.4_8	600	0.369	5.30	1.05_5
11-40	3	Tank	50.3	14.4_8	1080	0.602	4.97	0.98_8
12-41	5	Tank	106.2	26.6	1080	0.426	5.85	0.55_1
14-45	6	White Pine	38.4	11.1_6	600	0.498	7.15	1.86_1
15-47	4	White Pine	56.4	16.1_6	600	0.529	7.86	1.39_5

TABLE 3

(Continued)

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Time Base (min.)	(7) Average Slope	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
16-49	6	White Pine	84.4	22.5	600	0.395	9.10	1.07_9
20-57	8	Tank (Unscrubbed)	38.7	11.26	600	0.319	4.58	1.18_4

in all subsequent experiments. Here gas was admitted to the chamber until the desired gauge reading was attained. Addition of the barometric pressure to the gauge pressure converted the latter to absolute pressure, which is the value tabulated in column (5). The gas in the chamber and manifold was allowed to come to room temperature before the chamber valve was closed. As this temperature was generally within a few degrees of 20° C. the pressures were converted to gms. of CO_2 by use of van der Waals' equation at 20° C. This limits the accuracy of the data to about 1%, but this was considered sufficient for these experiments. The voltage calibration factors used in calculating column (8) were as follows: experiments 10b, 11-38 and 14 = 3.85 v./div.; experiments 11-40 and 15 = 3.98 v./div.; experiment 16 = 6.17 v./div. The slopes in experiment 12 were measured with the travelling microscope, and the two calibration factors were 1.89 cm./1080 min. and 78.9 v./cm.

Using the values of I_s at 40 gms. of CO_2 for comparison it is evident from Figures 7 and 8 that the background ionization in Morris Dam is less than half of that in the "astropit". The ratio of the ionization due to the sample activity to the background ionization improved from 0.25 to 0.32. It appears from these figures that the ionization due to the carbon-14 in the wood has decreased. However, the effect is probably accounted for by uncertainties in the voltage calibration factors used, as previously noted.

Additional experiments were carried out in the dam to make some estimate of the suitability of the method for age determination. The samples used were cones from the tree pseudotsuga macrocarpa, anthracite coal and specimen No. 2997 from the collection of Mr. Harold Gladwin.

The average age of this log has been determined to be 1,830 years by an elegant tree ring counting technique developed by Mr. Gladwin. By this time the second ionization chamber (No. 2) was in working order and some measurements of these samples were made with it. Table 4 gives the results with instrument No. 1 and Table 5 the results with instrument No. 2. The pressure gauge filling method was used in all cases. The time base with instrument No. 1 was 600 minutes and with No. 2 it was 720 minutes. The voltage calibration factors were 3.85 v./div. and 4.68 v./div., respectively.

A discussion of the main sources of error is in order at this point. One possible source of error in any given experiment is impurities in the chamber filling. The inclusion of small quantities of electronegative substances, such as, O_2, NO or H_2O would have the effect of increasing the volume recombinations and thus decrease the rate of discharge of the electroscope. It is believed that the CO_2 when prepared and stored in the small cylinders contains much less than 0.1% of any such impurity. The possibility exists that some air might enter the chamber on pumping it out or that the evacuation might not have been complete but is considered highly unlikely. That the chamber possesses no "memory" is proved by the fact that a filling of tank carbon dioxide following the $C^{14}O_2$ sample showed no increase in rate of discharge over the value obtained prior to the active filling. Errors in the timing motor and gears should be negligible. It is well known that photographic film can change its dimensions as much as 2-3% with changes in humidity. The change should be the same in all directions, and thus the slopes would be altered by a smaller amount. An error of 1% from this source is not unreasonable,

TABLE 4

Instrument No. 1 in Morris Dam: Age Determination

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Average Slope	(7) Average Deviation of Mean	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
21-58	11	Pine Cones	38.4	11.18	0.530	0.002	7.61	1.96_6
24-62	10	Pine Cones	38.4	11.18	0.513	0.001	7.37	1.92_0
23-61	7	Anthracite	38.4	11.18	0.385	0.004	5.53	1.43_9
25-63	9	Anthracite	38.4	11.18	0.351	0.002	5.04	1.31_6
17-52	4	No. 2997	38.7	11.26	0.459	0.001	6.65	1.71_8
22-60	10	No. 2997	38.4	11.18	0.470	0.002	6.75	1.75_8

TABLE 5

Instrument No. 2 in Morris Dam: Age Determination

(1) Exp't. and Film No.	(2) No. of Traces	(3) Source of CO_2	(4) Wt. of CO_2 (gms.)	(5) Pressure at 20° C. (atm.)	(6) Average Slope	(7) Average Deviation of Mean	(8) $I_v \times 10^2$ (v./min.)	(9) $I_s \times 10^3$ (v./min./gm.)
209-220	8	Pine Cones	38.7	11.26	0.794	0.004	11.56	2.98_8
211-223	6	Pine Cones	38.4	11.1_8	0.741	0.002	10.79	2.80_9
207-218	18	Anthracite	38.4	11.1_8	0.499	0.003	7.26	1.89_0
208-219	9	Anthracite	38.4	11.1_8	0.497	0.003	7.23	1.88_2
212-224	7	Anthracite	38.4	11.1_8	0.500	0.003	7.28	1.89_5
210-222	10	No. 2997	38.6	11.2_2	0.673	0.003	9.80	2.54_0

however. Similar changes are possible in the size of the piece of graph paper used to read the slopes, although this was well cemented to a piece of Masonite. As mentioned above the pressure gauge used was claimed to have a precision of 1/2 of 1%. An error of similar magnitude is involved in van der Waals' equation, and if temperature variations are considered the total filling error lies between 1 and 2%. Undoubtedly the weighing technique is superior in accuracy, although somewhat less convenient. At any rate this filling error can be reduced in future work. It is obvious from the data in Tables 4 and 5 that in two cases the disagreement between corresponding I_s values is considerably greater than the total error of 2-3% described above. In other cases the agreement between the results obtained from different fillings from the same source is excellent. At this writing it cannot be said that the possibility of some instrumental malfunction has been entirely eliminated. However, the data do substantiate Libby's contention that the activity of carbon from specimens of archeological age is less than that of recent carbon.

From the data in the tables the age of sample No. 2997 can be directly calculated by the following modification of the usual radioactive decay equation:

$$I_s^{2997} - I_s^{\infty} = (I_s^{o} - I_s^{\infty})\, e^{-\lambda t} ,$$

where I_s^{2997} is the specific rate of discharge of the electroscope with sample No. 2997 in the chamber, I_s^{∞} is that with anthracite coal and I_s^{o} that with pine cones. λ is the decay constant of carbon-14 and is equal to 0.693 divided by the half-life of that activity. Two very careful investigations of this half-life have been published recently. The values obtained are 5720 ± 100 years (20) and 5589 ± 75 years (21). Since

both sets of workers used essentially the same method and both results appear equally trustworthy the average of the two, 5,655 years, will be used here. Using the data obtained with instrument No. 1 and taking the average values of the various I_s's, the age of sample No. 2997 is calculated to be 3,700 years. The age as similarly determined from the data of instrument No. 2 is 3,550 years. Despite the fairly good agreement between these values it cannot be said that the uncertainty in either is less than 1,000 years. Even with this large error the age of the specimen is in rather violent disagreement with the age as determined on the basis of tree ring counting. The difference between the two is far outside any conceivable experimental error in either method. Further experiments will doubtless resolve the enigma.

Discussion

It is clear that any problem involving the measuring of small activities soon resolves itself into a fight to lower the background. With the ionization chamber method of measurement there are three sources of ionizing radiation which contribute to the background ionization of the chamber. These are cosmic radiation, gamma emitting radioactivity in the immediate surroundings and alpha particle emitters in the walls of the chamber. Making use of the data already tabulated and, in addition, the result of one additional experiment, the contribution from each of the three sources can be estimated. The discussion will be limited to the background ionization observed in Morris Dam with instrument No. 1.

By plotting the total rate of discharge of the electroscope against pressure or amount of gas in the chamber and extrapolating the plot to

zero pressure a good estimate of the ionization due to alpha particles from the walls is obtained. The extrapolation essentially eliminates the ionization in the chamber caused by radiation, which completely traverses the chamber, i.e., mesons and the great majority of the gamma rays from the surroundings. Figure 9 presents such a plot. Pressure instead of mass was plotted along the axis of abscissas as a matter of convenience, the difference not being significant in this case. The intercept on the axis of ordinates is 4.26×10^{-2} v./min. On the assumptions that this effect is entirely due to emission of alpha particles of an average energy of 5 mev. and that the mean energy lost per ion pair formed by the collisions of the particles with CO_2 molecules is 32.5 e.v., a calculation similar to that on page 101 of this thesis gives 1.0 alpha particles per minute being emitted into the chamber. The radius of the chamber being 7.5 cm. this amounts to 2 alpha particles/sq. cm./day. This value is in good agreement with the results of Bearden's experiments on the contamination of ionization chamber walls (22). The lowest alpha emission rate which he was able to obtain was 0.8 alphas/cm.^{2}/day, and this with machined cold rolled steel which was kept from exposure to air. The treatment of the walls of the chambers used in the present experiments was as follows: The chambers (of commercial steel) were copper plated and then nickel plated over this. A thick coat of a conducting paint of lamp black and collodion was then applied to the inside walls. This last treatment reduced the alpha particle contamination by about a factor of one-tenth (17). No precautions were taken to avoid exposure to air, however. It would seem that a significant further decrease in this effect might be achieved by an appropriate treatment of the chamber walls.

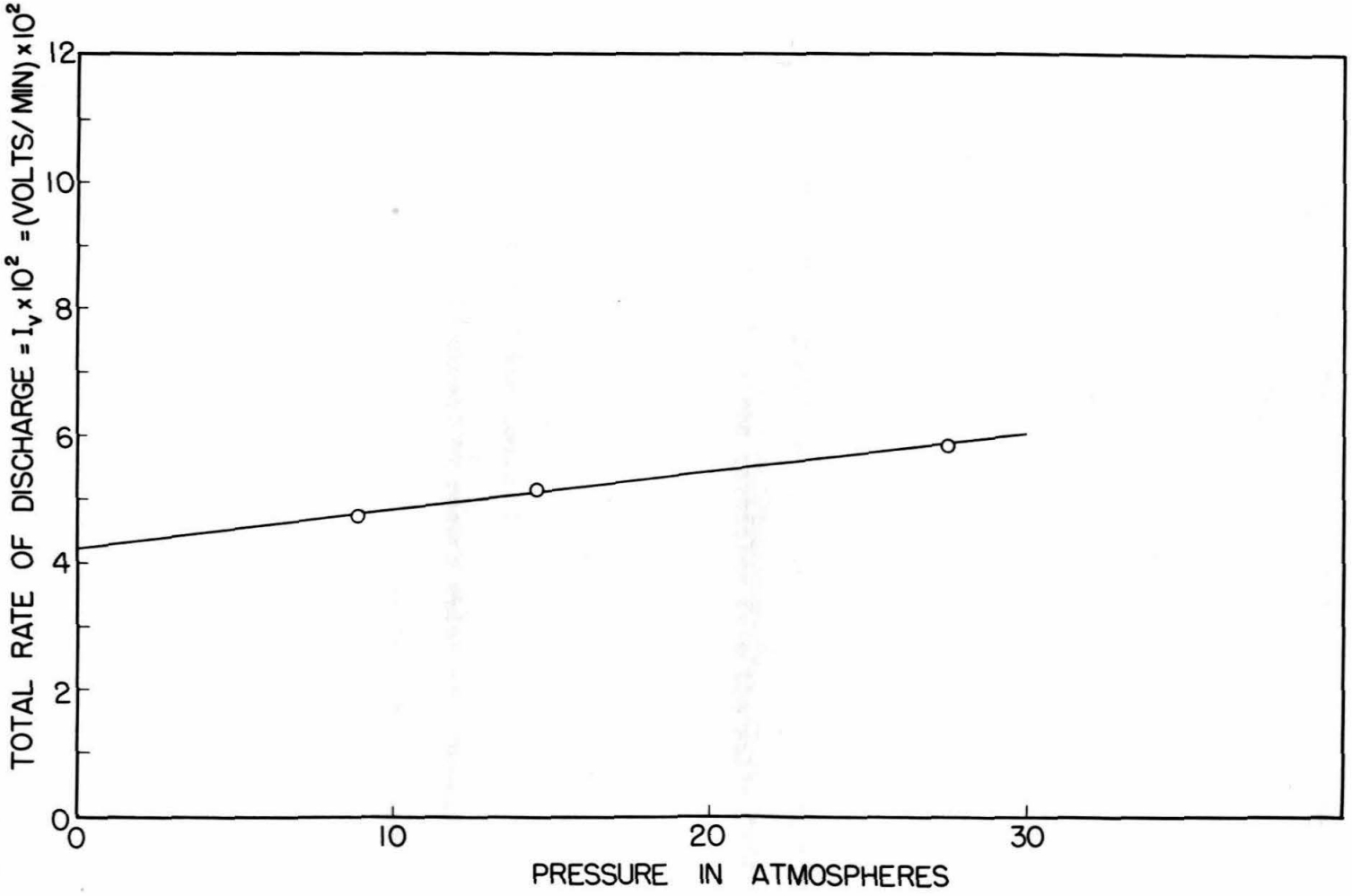

FIGURE 9.
TOTAL DISCHARGE RATE VS. PRESSURE
INSTRUMENT NO. 1 IN MORRIS DAM
TANK CARBON DIOXIDE

Inspection of Figure 9 reveals that at 11 atm. the alpha particles contribute 87% of the total background ionization. In an effort to identify the other 13% a run was made in the dam with the chamber removed from the lead shielding. The latter, being 15 cm. (4") thick, should reduce the gamma radiation intensity to 0.6% of the unshielded value (17). In the experiment mentioned the rate of discharge of the electroscope increased by a factor of 26 when the shielding was removed. By a direct calculation it is seen that the gamma radiation contribution to the background amounts to 15%. Thus to within the accuracy of these calculations - about 1% - the background ionization in Morris Dam is due entirely to the alpha particles from the walls (86%) and the gamma radiation from the surroundings (14%). That the contribution from cosmic radiation should be small has been seen from a consideration of the amount of shielding afforded by the dam and lake. It is possible that some of the ionization ascribed to gamma radiation in the above calculation is caused by mesons which are stopped in the lead shielding. However, it is unlikely that any great fraction of the particles which penetrate the concrete of the dam will be stopped by the 4" of lead. It should be noted that the concrete of the dam is undoubtedly more radioactive than the surroundings about most localities in which one would carry out radioactivity measurements (17). It is estimated that a reduction of this contribution by a factor of as much as one-sixth is possible with a careful choice of locations.

Having available the above information regarding the background effects makes it possible to estimate the statistical reliability of the carbon-14 measurements. The general problem of the statistical

fluctuations incident to ionization chamber measurements has been treated by R. D. Evans and H. V. Neher (23). They give the following expression for the square of the mean deviation, D, of the combined effect of several random processes releasing an average of x, y, z..... particles per unit time and producing a, b, c..... ion pairs, respectively per particle:

$$D^2 = a^2 x + b^2 y + c^2 z + ...$$

For the problem at hand the following identifications are made:

x = no. of C^{14} beta particles/min.

y = no. of gamma rays/min.

z = no. of alpha particles/min.

a = 1.5×10^3.

b = 10^3 for average gamma ray produced electron.

c = 1.5×10^5 for 5 mev. alpha particles.

With 33 grams of live CO_2 in the chamber, x = 90, y = 20* and z = 1. Using these figures we get

$$D^2 = 2.3 \times 10^6 \times 90 + 20 \times 10^6 + 2.3 \times 10^{10} = 2.3 \times 10^{10}$$

and

$$D = 1.5 \times 10^5.$$

It is evident that the fluctuations produced by the alpha particles predominate over the other sources. In fact the C^{14} effect is just above the natural observational limit, i.e., it is about equal to the probable

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* This figure was determined by a calculation similar to that used to obtain the alpha particle contamination and using 10^3 as the average number of ion pairs formed by the gamma ray produced electrons.

statistical variation in the background. This limit is r = 0.67 D = 1 x 10^5 ions/min. The ionization due to the C^{14} is 1.4 x 10^5 ions/min., only slightly above the statistical variation in the alpha particle background ionization. The only way to overcome this rather serious limitation on the precision of the measurements is to use long counting times. If a standard deviation of 1% (larger than the value actually observed) is desired the time of counting can be calculated thus:

$$\sigma = 1\% = \frac{1}{\sqrt{t}} \times D, \text{ where t is the counting time.}$$

$$t = D^2/\sigma^2 = 2.3 \times 10^{10}/0.0001 \times 2 \times 10^{10} = 1.1 \times 10^4 \text{ minutes.}$$

Actually average deviations of 0.5% and less were observed for counting times of about 6,000 minutes. The explanation of this lies in two factors. First, considerable columnar recombination along the alpha particle tracks will reduce the effective number of ion pairs formed per particle. That such recombination does take place is shown by the trend of the I_s vs. gms. of CO_2 curves (Figures 7 and 8). The second factor is simply that the assumed average energy of the alphas is certainly too large. This value is a rough average of the energy of the alphas emitted by uranium and the decay products in equilibrium with it. Since the particles will be emitted from varying depths the average energy of the particles on reaching the chamber will be considerably less than 5 mev., and hence the number of ion pairs per particle will be smaller than the value used. An inevitable conclusion from the above argument is that the number of alphas emitted from the wall is actually larger than the 1 per minute previously calculated. Assuming that the combined effects (recombinations and reduced energy of emission into the

chamber gas) reduce the average number of ion pairs formed per alpha by a factor of ten, and consequently increase the number of particles by the same factor, an average deviation can be calculated. The result obtained for a 6,000 minute count is 0.47%, very close to the actually observed deviations. The rate of emission of alpha particles to which this corresponds, about 20 cm.^{2}/day, is within reason but higher than expected.

It is instructive at this point to calculate the average deviation, D, for the ionization chamber operating in the "astropit". To do this it is necessary to add the effect of the ionization due to cosmic ray mesons. For a specific ionization of 100 ion pairs/cm./atm. and an average path length of 10 cm. the average number of ion pairs per meson is seen to be 10^4. The observed increase in ionization is 6.8×10^{-2} v./min., corresponding to 2.4×10^5 ions/min. Thus about 24 mesons pass through the chamber per minute. From this and the values used for the chamber in Morris Dam one obtains

$$D^2 = 2.25 \times 10^6 \times 90 + 2 \times 10^8 + 2.3 \times 10^{10} + 24 \times 10^8$$
$$= 2.5 \times 10^{10}.$$

One concludes from this that no great advantage as far as statistical reliability is concerned is gained by working in Morris Dam. However, in the event that the alpha particle contribution can be decreased the shielding from cosmic radiation afforded by Morris Dam will result in a considerable gain in precision.

In conclusion some consideration will be given to possible ways of improving the method and also to significant experiments which should be carried out. At first thought it might seem that the effect could be

made more pronounced by working at higher pressures, i.e., putting more CO_2, and hence more $C^{14}O_2$, into the chamber. This would have the additional beneficial effect of reducing the alpha particle contribution through increasing the recombinations along the alpha tracks. That this approach is fruitless can be seen from Figure 8. The two curves are approaching one another at higher pressures, probably because the recombination of the ions along the C^{14} beta particle tracks is increasing with pressure. The average deviation calculations above make it clear that the most profitable approach is to reduce the number of alphas emitted from the walls. At this point certain suggestions can be made along this line. First, the lampblack paint possibility should be thoroughly investigated. In this connection the chambers should be cleaned and painted in an argon atmosphere if possible. Second, the effect of metal coatings should be studied. There is no a priori reason why some pure metal, such as gold, silver or nickel, when deposited on the chamber walls by evaporation or "sputtering" or other processes, should not be quite free of alpha emitting contaminants. If none of these approaches is successful a chamber with a screen or grid wall could be constructed. A reduction in area by a factor of at least 50 is possible. One other method of improving the "signal to noise ratio" is to construct a larger chamber, thus increasing the volume to surface ratio. This approach will be tried soon along with a new electroscope and recording system designed by Professor H. V. Neher.

Another question which can and should be settled by appropriate experiments is the efficiency of the ion collection in CO_2 at high pressures. The extent of volume recombinations could be determined by

carrying out experiments at varying rates of ionization at one pressure to see if the effects are additive. Another way of investigating this point would be to see if the rate of discharge of the electroscope is strictly proportional to pressure at rates of ionization high enough to make the wall effect negligible.

In conclusion it can be said that, while fundamentally sound, the ionization chamber technique cannot as yet be considered a reliable dating method.

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PART V

THE VOLUME CHANGE DUE TO HYDROGEN BONDING OF METHANOL IN CARBONTETRACHLORIDE SOLUTION

Introduction

The association of alcohols through hydrogen-bond formation is well known (1, 2, 3). In this connection one of the systems, which has been extensively studied, is the solution of methanol in carbontetrachloride. The results of the many investigations of the physicochemical properties of these solutions generally can be explained on the basis of the marked tendency of methanol to associate into polymers. R. Mecke and his co-workers have shown that only in extremely dilute solutions is there an appreciable fraction of the monomer, CH_3OH (4, 5, 6). The evidence presented in these papers is mainly spectroscopic. In this method Beer's law is applied to the intensities of the OH band at 10,450 $cm.^{-1}$ to obtain the concentration of the monomer. This particular band is observed in the gas phase but not with the pure liquid or concentrated solutions, and thus it is assumed that the band disappears entirely on association of the CH_3OH molecules and that its intensity is a measure of the concentration of monomer. The last paper of Mecke's (6) also gives some vapor pressure data which are in excellent agreement with the spectroscopic evidence.

Since the assumptions on which the spectroscopic method is based are open to question, consideration was given to other physical properties of dilute solutions of methanol in carbontetrachloride which might throw

some light on the question of the extent of association of the CH_3OH molecules. It appeared that the partial molar volume of the methanol might be one such property. A search of the literature revealed that while many data on the densities of solutions of methanol in carbontetrachloride exist no attempts had been made to derive partial molar volumes from these, and, in particular, no correlation of the data with the spectroscopically determined extent of association had been made. Accordingly a sensitive Westphal balance was constructed for the determination of the densities of CH_3OH-CCl_4 solutions. By incorporating in the device a micro-buret it was possible to prepare a continuous series of very dilute solutions of methanol in carbontetrachloride while maintaining an essentially closed system. The precision of the density measurements was better than one part in 10,000. In addition to the data thus obtained the best density data on this system have been extracted from the literature and included in the argument.

Experimental

Reagent grade carbontetrachloride was distilled twice, once from solid KOH and the second time from fused $CaCl_2$. The boiling range, corrected to 760 mm., of the second distillation was 76.7 to 76.9° C. Reagent grade, special methanol was used with no further purification. The assay on the sample used claimed less than 0.1% other organic substances and about 0.4% water.

The Westphal balance was constructed from a precision analytical balance. One pan was removed and a solution cup with a thermostating jacket mounted under the hanger. This apparatus is diagrammed in Figure 1.

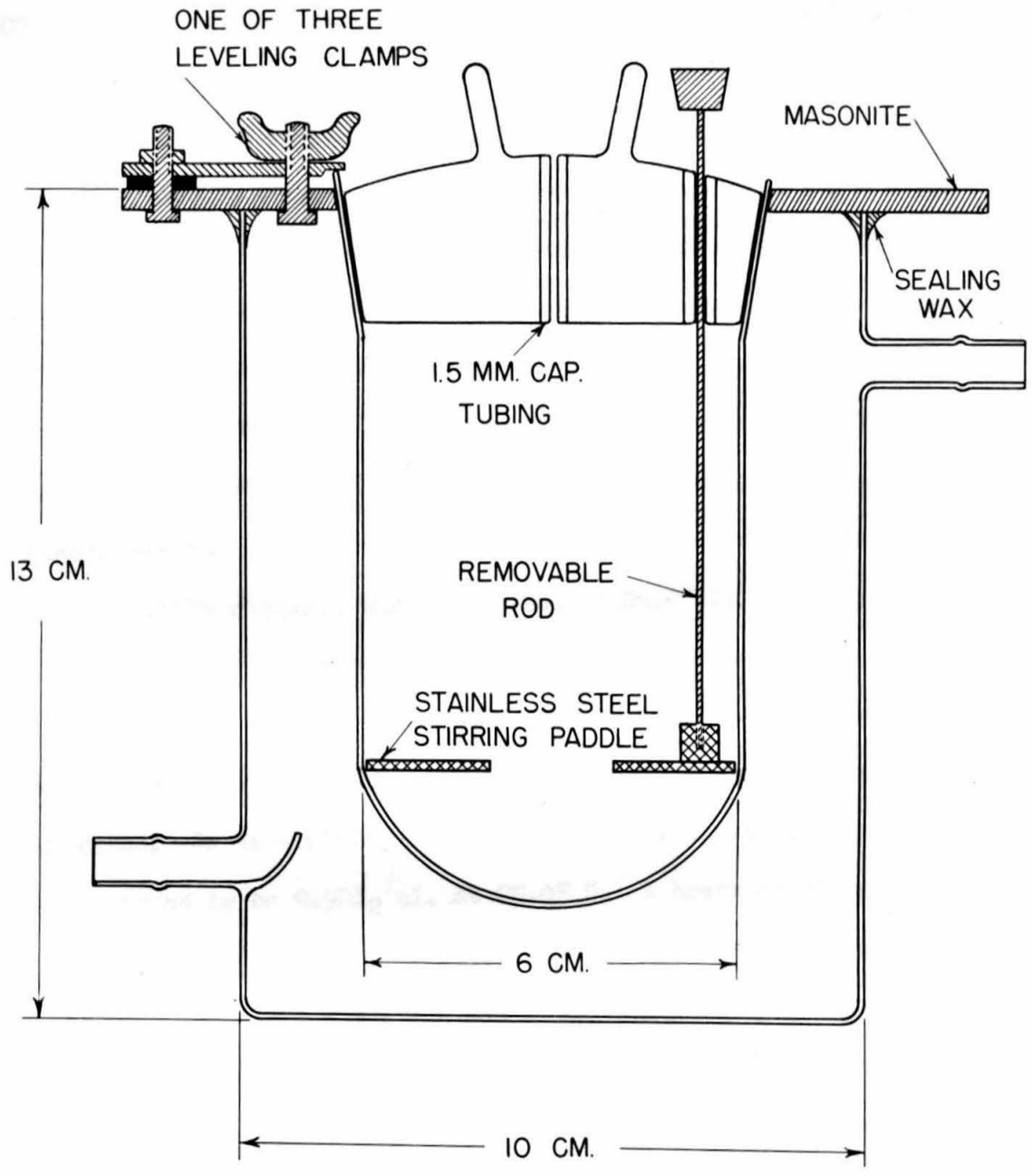

FIGURE 1.
SOLUTION CUP AND JACKET
FOR WESTPHAL BALANCE

An 800 ml. beaker with a masonite ring waxed to the top constituted the jacket. The solution cup fitted snugly into the hole in the ring and was levelled by means of three equally spaced clamps as shown. Thermostating was achieved by running tap water through a tube containing a nichrome heating coil. By careful regulation of the flow of water (a needle valve was used) and the current through the heating coil it was possible to maintain a temperature of about 25° C. within 0.2° C. for several hours and to within 0.05° C. for 0.5 hr. Since it was difficult to set the temperature precisely at 25.0° C. an empirical temperature correction factor was determined for several concentrations of methanol. Using this all the readings were corrected to 25.0° C.

The sinker was made from an ordinary test tube and had an outside diameter of 1.8 cm. and a length of about 5 cm. An appropriate amount of mercury was sealed into the sinker to increase the weight to 20.2656 gms. in vacuo. By determining the weight in boiled distilled water the volume was found to be 9.981_2 ml. at 25.0° C. A brass counter weight was suspended from the hanger to compensate for the weight of the pan which had been removed. From the bottom of this weight the sinker was suspended with a weighed length of 46 B & S gauge nichrome wire. The wire was passed through the 1.5 mm. capillary tubing in the center of the ground glass stopper of the solution cup. With the sinker immersed in CCl_4 the rest point of the balance was easily reproducible to 0.2 mg. Damping did not interfere with the weighings in any way. The "pull" due to surface tension on a clean wire of this size is about 0.4 mg. No correction was applied for this as it should be a constant factor, affecting the absolute values very little and the relative values not at all.

As mentioned above a micro-buret was incorporated into the apparatus to facilitate the preparation of a series of solutions of varying CH_3OH concentration, without having to remove the stopper from the solution cup. The buret was of the syringe type described by Shaffer, Farrington and Niemann (7). It was calibrated with water, and the scale was found to be reliable from 0 to 2.000. The volumes delivered were reproducible to 0.001 ml. One full scale division corresponded to 0.723 ± 0.001 ml. at about 25° C. The buret was mounted horizontally in the balance case, and the methanol was delivered to the solution cup through a long hypodermic needle with a right angle bend. The end of the needle was passed through the off-center capillary tube in the stopper (rod removed).

In a typical series of determinations the operations were carried out as follows: The stirring paddle was placed in the cup. The sinker was suspended through the center capillary of the stopper. With a carefully calibrated (with CCl_4) 100 ml. volumetric pipet 200 ml. of CCl_4 were transferred to the cup. The stopper was immediately put in place and the cup levelled beneath the hanger. Care was taken, of course, to see that the suspension did not touch the sides of the capillary tube. The rod was passed through the other capillary and screwed into the stirring paddle. Approximately ten minutes were allowed for thermal equilibrium to be established. During this period the liquid was gently stirred occasionally. The weight of the sinker in the CCl_4 was determined - the average of about three readings being used in the subsequent calculations - and the temperature of the water in the jacket recorded. After this the micro-buret, filled with methanol, was

lowered until the hypodermic needle tip was just below the surface of the liquid (stirring rod removed, of course). The desired amount of liquid was added to the solution and the buret tip removed from the solution. With the rod replaced the solution was stirred about ten times and another ten minutes allowed for establishment of thermal equilibrium. The weight of the sinker was determined and then the whole process was repeated. In this way the densities of ten to fifteen solutions varying from 0.04 wt. % CH_3OH to about 5% CH_3OH were determined. The amount of alcohol added was calculated from the volume delivered and the density at the temperature of the balance case (8). The combination of the temperature uncertainty, 0.02° C. = 0.3 mg., and the weighing error, 0.2 mg., produced a total uncertainty in each weighing of about 0.5 mg. Since the total weight of the sinker in the liquid was about 5 gms. the precision of the measurements was limited to about 0.01%. As an indication of the accuracy of the device it can be stated that the value obtained for the density of pure CCl_4 at 25° C. checks with the best literature values to one part in 15,000.

Results and Discussion

The results of the one reliable series of determinations - made after the technique was finally mastered - are given in Table 1. To convert these density data into partial molar volumes the method of apparent specific volumes was used (9). The apparent specific volume of component 2 of a binary solution is defined by

$$\tilde{V}_2 = \frac{V - z_1 \bar{V}_1^{\circ}}{z_2} ,$$

TABLE 1

Density of Solutions of Methanol in Carbontetrachloride at 25° C.

Weight Fraction of CH_3OH	Density at 25° C. (gms./ml.)
0	1.58445
0.0358	1.5838
0.0717	1.5833
0.1076	1.5828
0.1431	1.5821
0.1785	1.5817
0.3562	1.5787
0.5332	1.5757
0.7096	1.5730
0.8853	1.5701
1.0605	1.5673
2.255	1.5485
3.422	1.5309
4.558	1.5140
5.673	1.4979
6.758	1.4825
7.995	1.4655
14.270	1.3852
33.190	1.1871

where Z_i is the weight fraction of component i, $\bar{V}_1^o$ is the specific volume of the pure substance 1 and V is the measured specific volume of the solution. It can readily be shown that

$$\bar{V}_2 = \tilde{V}_2 + Z_1 \frac{\partial \tilde{V}_2}{\partial \ln Z_2},$$

where $\bar{V}_2$ is the partial specific volume of component 2. In practice the apparent specific volume of the component of interest is plotted as a function of the logarithm of the weight fraction of that compound. The partial specific volume at any given concentration is then equal to the sum of the ordinate and Z_1 times the slope of the curve at that point. Multiplying the partial specific volume by the molecular weight gives the partial molar volume, of course. Figure 2 presents such a plot of apparent specific volumes - calculated from the data in Table 1. The probable errors are shown by the vertical lines through the points. These errors include the uncertainty in the density and in the weight fractions. Since the calculation involves a difference method the errors are much greater in the region where the differences are small.

In addition to the data from these experiments two other sources were used and the apparent specific volumes calculated therefrom are plotted on Figure 2. Scatchard, Wood and Mochel used a pycnometric method in their work and the values obtained by them should be very reliable (10). Harms constructed an exceedingly elaborate Westphal balance for his measurements and claims an accuracy of three parts in the seventh decimal place (11). Unfortunately he includes no numerical

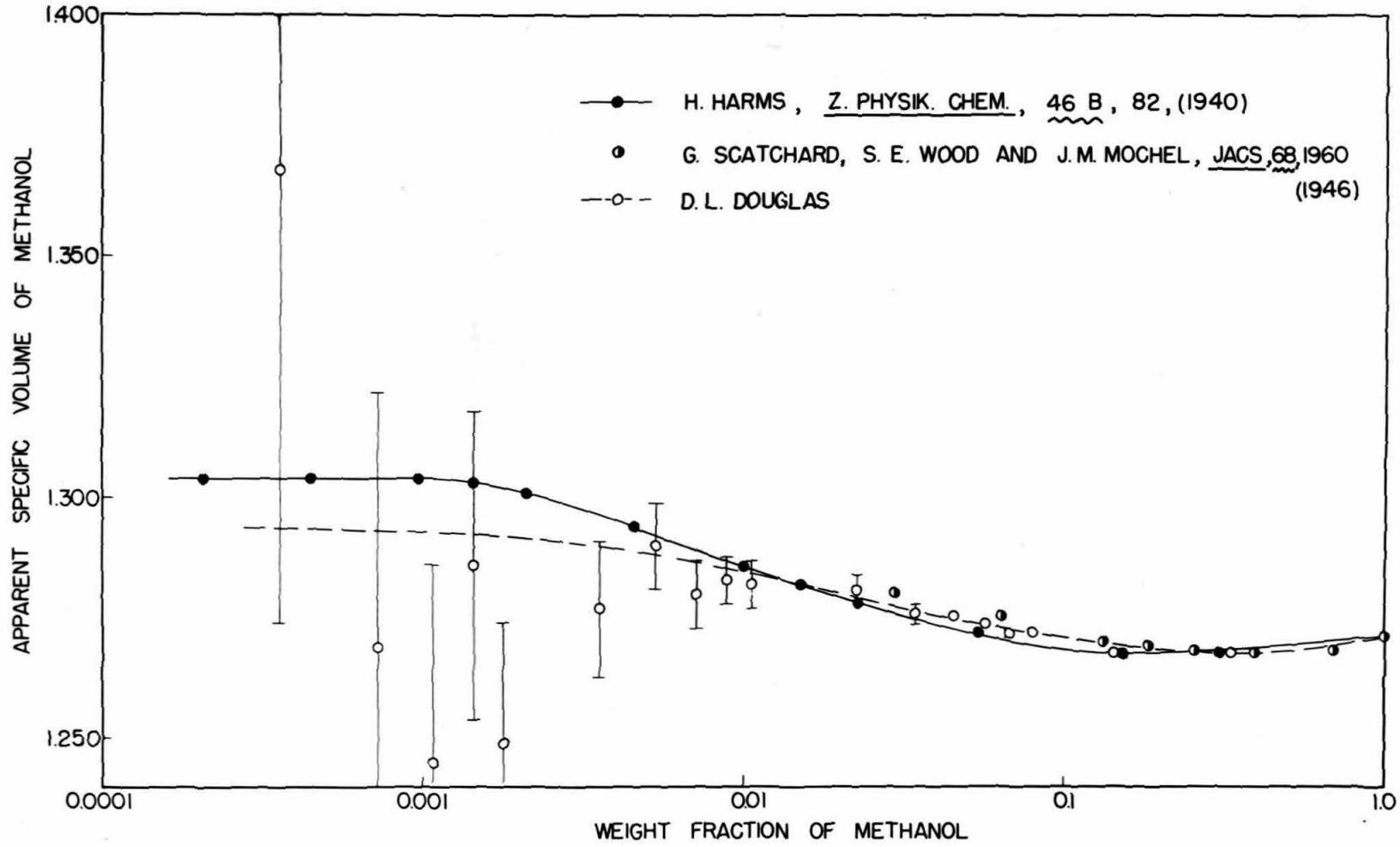

FIGURE 2.

APPARENT SPECIFIC VOLUME OF METHANOL IN CARBONTETRACHLORIDE

data whatsoever in his paper. One small plot of $\Delta V_M = \frac{V^{ber.} - V^{exp.}*}{X_2}$ against X_2, the mole fraction of CH_3OH, is presented. Since there are no plotted points, it is necessary to assume that such data as were obtained by Harms were smoothed in the drawing of the curve. In fact it is necessary to assume that the negative, $-\Delta V_M$, was actually plotted in order to make any sense at all out of the curve. With a pair of dividers and a scale a series of values of ΔV_M were obtained from this curve. These were converted to apparent specific volumes by means of the relation $\tilde{V}_2 = V_2^o - \frac{\Delta V_M}{M_2}$, and the values obtained plotted as points on Figure 2.

Regarding the data obtained in the experiments performed by the writer it is obvious that the points scatter greatly in the region of most interest. The most that can be said is that they do not disagree violently with the results of Harms. It should be noted that when the work was started a much greater effect was expected, and the apparatus was considered to be sufficiently sensitive. If the points suggest anything at all they suggest that the apparent specific volumes should be smaller than reported by Harms in the region of low concentration. In order to see what the effect on the final values of the partial molar volumes would be one curve (dashed line) was drawn in Figure 2. That the curve must level out and not turn downward can be justified as follows: As Z_2 approaches zero, Z_1 approaches unity and $Z_1 \frac{\partial \tilde{V}_2}{\partial \ln Z_2} = Z_1 Z_2 \frac{\partial \tilde{V}_2}{\partial Z_2}$

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* $V^{ber.}$ is the volume calculated for strict additivity of the volumes of the components, and $V^{exp.}$ is the observed volume.

approaches zero. Thus the apparent specific volume approaches the partial specific volume as a limit at $Z_2 = 0$, and the trend of the curve in this region is parallel to the weight fraction axis. If the reasonable assumption is made that the partial specific volume is a monotonic function of Z_2 in this region, then the curve must be drawn somewhat as shown.

Table 2 gives the partial molar volumes obtained from the two curves in Figure 2. For the region of interest, i.e., low concentration, the partial molar volumes are plotted as a function of mole fraction of methanol in Figure 3. The points correspond to the results tabulated in Table 2. In addition the fraction of the CH_3OH present in monomeric form, from spectroscopic data, is shown as a function of concentration. The points on this last curve were taken from a somewhat similar plot in the last paper by R. Mecke (6).

It is clear from an inspection of the curves that the partial molar volume of the methanol is changing in manner proportional to the amount of monomer in the solution. To further test this proportionality the partial molar volumes have been plotted as a function of fraction of monomer in Figure 4, the points representing merely values taken from Figure 3. Evidently both the data obtained in these experiments and that from Harms' paper show the volume change to be nearly linear with change in monomer fraction in the low concentration region. From the former the total change in the partial molar volume on passing from the completely polymerized methanol to the monomer is about 0.8 ml., and from the data of Harms the volume change is about 1.1 ml. The agreement between the two results is considered satisfactory.

The linear relationship between the partial molar volume and the

fraction of monomer implies, of course, only that the methanol molecules are about 2% smaller on the average when joined together as polymers by means of hydrogen bonds. Since the polymers might not pack so well in the CCl_4 solution this resultant volume change may well be only the difference between the actual decrease in size of the molecule and this packing effect. Thus the actual change in volume occupied by the methanol molecules may be considerably greater than the 2% observed. It being impossible to estimate the magnitude of the packing effect it can be said only that the increase in the volume of a mole of CH_3OH on going from polymer to monomer is at least 1 ml.

TABLE 2

Partial Molar Volume of Methanol in Carbontetrachloride at 25° C.

Wt. Fraction CH_3OH	Mole Fraction CH_3OH	Partial Molar Volume (D.L.D.) (ml.)	Partial Molar Volume (H.H.) (ml.)
1.00	1.00	40.72	
0.60	0.878	40.72	
0.30	0.673	40.66	
0.20	0.546	40.59	
0.10	0.348	40.61	
0.06	0.235	40.66	
0.03	0.129	40.72	
0.02	0.0892	40.82	40.69
0.01	0.0462	40.98	40.92
0.007	0.0327	41.08	40.98
0.006	0.0281	41.11	41.04
0.005	0.0236	41.14	41.11
0.004	0.0189	41.20	41.17
0.003	0.0142	41.27	41.30
0.002	0.0095	41.30	41.46
0.001	0.0048	41.40	41.78

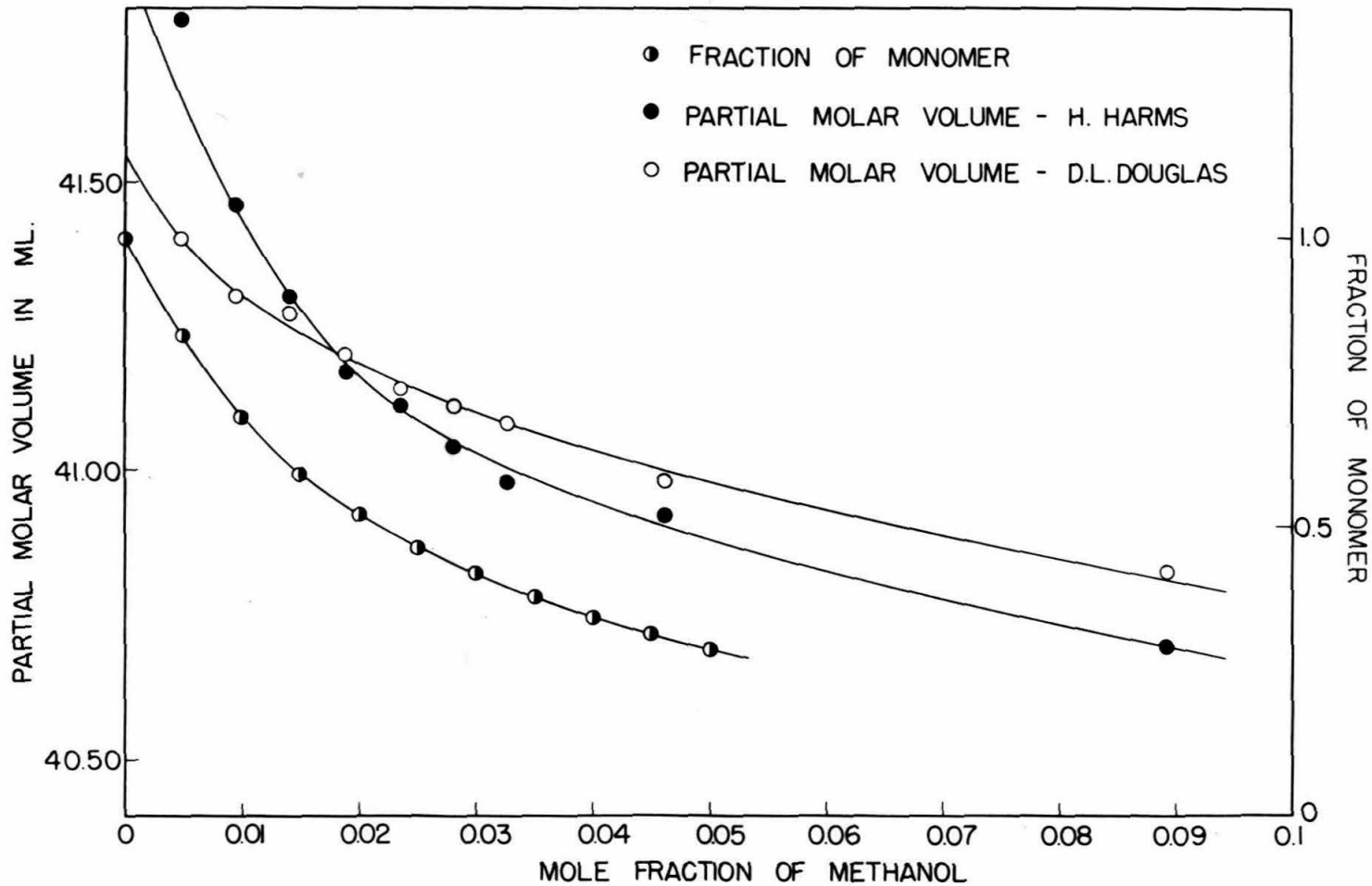

FIGURE 3.
PARTIAL MOLAR VOLUME AND MONOMER FRACTION OF METHANOL IN CARBONTETRACHLORIDE

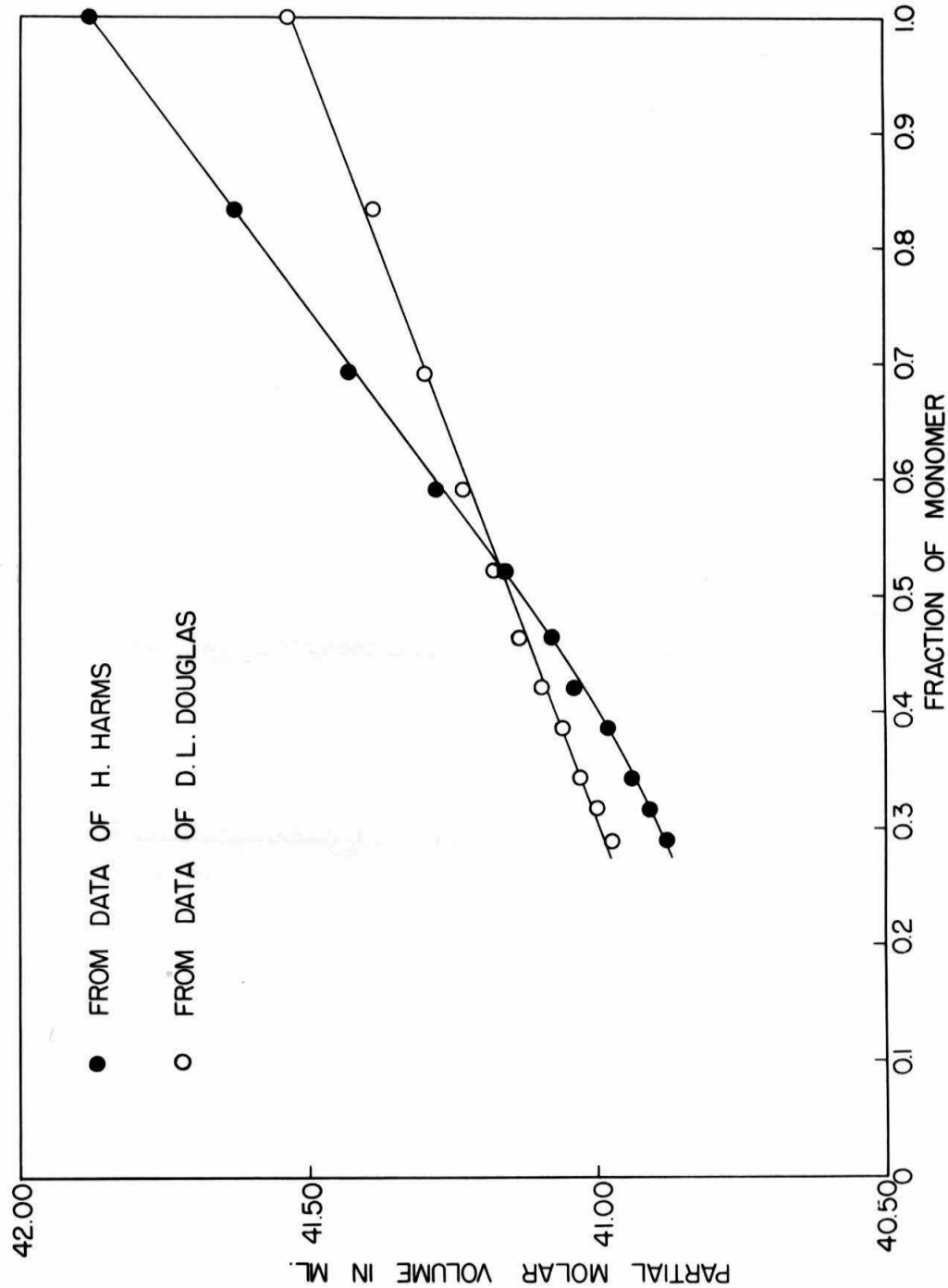

FIGURE 4.
PARTIAL MOLAR VOLUME OF METHANOL IN CARBONTETRACHLORIDE
VS. FRACTION OF MONOMER

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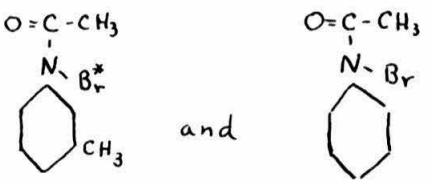
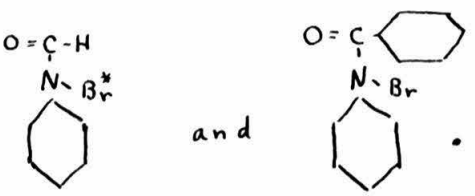
PROPOSITIONS

1. The molecular rearrangement of aryacylhalogenoamines into o- and p- halogenoacylamines in solvent media is well known (1, 2, 3). It has been reported that this rearrangement, photochemically stimulated, also takes place in the solid state (4, 5). An intramolecular mechanism has been suggested but by no means proved. The extent to which this intramolecular mechanism actually contributes to the rearrangement could be tested by means of a tracer experiment in two ways:

a. By using a mixture of  .

b. By using a mixture of  .

A separation of the aryl groups could be effected after rearrangement and the distribution of activity determined.

2. By the use of C^{14} and standard tracer techniques the sensitivity of the test for reduced carbon dioxide (see Part III C.) could be increased 10,000 fold. In addition tests for specific reduction products could be made with ease.

3. Such results as are available on the diamagnetic susceptibilities of solutions of associating liquids in non-polar solvents suggest that hydrogen-bonding may have a large effect on the diamagnetic properties

of the former (6, 7, 8, 9, 10). Magnetic measurements on very dilute solutions and with the vapors would provide valuable information in this regard.

4. The observation of Heal and Thomas (11, 12) that the "Becquerel effect" (13) can be used to reduce uranium(VI) sulfate solutions but not uranium(VI) chloride solutions can be explained on the basis of the quenching of the fluorescence of uranyl ion by chloride ion (14, 15, 16, 17). Experiments in which the chloride ion concentration is varied and also experiments to test the relative efficiency of chloride, bromide and iodide ions would verify this.

5. The following reduction systems are suggested for the preparation of samarium(II) compounds and possibly the rare-earth metals:
   a. Lithium aluminum hydride.
   b. Liquid ammonia solutions of the alkali metals. In this regard the possibility of preparing liquid ammonia solutions of the rare-earth metals should be investigated.

6. The existence of the substance sodium nitrosyl (NaNO) has been reported (18, 19, 20, 21, 22). There is some evidence that it is distinct from sodium hyponitrite, but the possibility that it is simply a more reactive form of the hyponitrite has not been eliminated. The question could be settled by investigations along these lines:
   a. Reactions with systems containing NO^+ ion (23).
   b. Careful determination of the structures of the compounds.
   c. More extensive search for a solvent for the sodium nitrosyl.

7. Over thirty years ago Söderbäck prepared the interesting compound nitrosyl thiocyanate (24), but since then the investigation of its properties has been almost completely neglected. Söderbäck found it to be stable in solution at -17° C. and observed that it has a deep red color. Seel postulates its structure to be NCSNO on the basis of a similar red color observed in nitrosyl mercaptides (25). In view of present knowledge concerning the structures of isocyanic acid (26) and isothiocyanic acid (27, 28) this structure is considered less likely than ONNCS. The following experiments are suggested:

   a. Attempts to isolate the pure compound.

   b. Attempts to prepare the analogous isocyanate compound.

   c. Study of the absorption spectrum (visible and infrared) as an aid in determining the structure.

8. The effect of strong magnetic fields on the rates of reactions (29, 30) involving paramagnetic substances should be studied in connection with the following reactions:

   a. Reduction of water by europium(II) ion.

   b. Reduction of water by vanadium(II) ion.

   c. Reduction of water by titanium(III) ion.

9. The information in the literature on recombination of ions in gases at high pressure is not adequate for reliable work with ionization chambers (31, 32). This problem should be systematically investigated with particular emphasis on the effects of small amounts of impurities.

10. Radioactive tracers would provide a simple means of extending the studies of specific adsorbents (33) to compounds analyses for which might be difficult by ordinary means.

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